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THE SYNTHESIS OF TRANS-DIMETHYLCOBALT(III) COMPLEXES OF TETRADENTATE MACROCYCLIC LIGANDS AND THEIR REACTIONS WITH METALLIC ELECTROPHILES

JEFFREY HOWARD DIMMIT

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To the three people who have most affected my life:

my parents, Howard and Jeanne Dimmit, and my wife, Suzanne.

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ABSTRACT

THE SYNTHESIS OF TRANS-DIMETHYLCOBALT(III) COMPLEXES OF TETRADENTATE MACROCYCLIC LIGANDS AND THEIR REACTIONS WITH METALLIC ELECTROPHILES

by

JEFFREY HOWARD DIMMIT

University of New Hampshire, December, 1980

The syntheses of two trans-dimethylcobalt(III) complexes are reported. The complex $[(CH_3)_2Co(Me_4[14]tetraeneN_4)]ClO_4$, where $(Me_4[14]tetraeneN_4)$ is the tetradentate macrocycle 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene that coordinates cobalt in a planar fashion with two conjugated α-diimines, was prepared by standard methods via the corresponding cobalt(I) derivative. The complex $(CH_3)_2Co([14]tetraenato(1-)N_4)$, where $([14]tetraenato(1-)N_4)$ is the tetradentate pseudo macrocycle 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-11-ol-1-olato that coordinates cobalt in a planar fashion with two conjugated α-imine-oximes, was also prepared by standard methods via the corresponding cobalt(I) derivative. The complexes were characterized by electronic, IR, and NMR spectroscopy.

The methyl-transfer reactions of the two dimethyl complexes with the metallic electrophiles, Zn^{2+}, Cd^{2+},

Pb^{2+}, Cr^{3+}, and Cu^{2+} in acetonitrile were studied. The organometallic products of these reactions are dependent upon the mole ratio of M^{2+}/dimethyl complex used. Reactions with the metal ion in excess produced monomethylcobalt(III) complex and an unstable CH_3M^{n+}.

When Zn^{2+}, Cd^{2+}, and Pb^{2+} were reacted with excess $(CH_3)_2Co(chel)$, the products were found to be dependent upon the metal ion used. The reaction of Zn^{2+} and Cd^{2+} with excess dimethyl complex yielded the dimethylmetal compounds, $(CH_3)_2Zn$ and $(CH_3)_2Cd$.

When Pb^{2+} was reacted with $(CH_3)_2Co([14]tetraenato-(1-)N_4)$, the intermediate $(CH_3)_2Pb$ disproportionated to yield $(CH_3)_4Pb$ and Pb^0 as the ultimate products. The reaction of Pb^{2+} with $[(CH_3)_2Co(Me_4[14]tetraeneN_4)]^+$ is unique. Approximately 75% of the Pb^{2+} added to this reaction was obtained as lead metal and 10% as $(CH_3)_4Pb$. The data obtained suggest that a complex mechanism not observed in the other demethylation reactions is in effect.

I. INTRODUCTION

Although the chemistry of cobalt-corrin compounds has been studied since the discovery of vitamin B_{12} in 1948 (1), it was Lenhert and Hodgkin's 1961 finding (2) that 5'-deoxyadenosylcobalamin (the coenzyme form of vitamin B_{12}) contains a cobalt-carbon bond which marked the initial interest in organo-corrinoids (see Figure 1). This interest has arisen for several reasons. The isolation of 5'-deoxyadenosylcobalamin marked the first discovery of an organometallic compound in a living system (3). Enzyme bound methylcobalamin has been shown to be an intermediate in the transfer of a methyl group from N^5-methyltetrahydrofolate (N^5-methylTHF) to homocystine in the biosynthesis of methionine (4) (eq 1 and 2). Other

$$N^5\text{-methylTHF} + \text{enzyme}\cdot\text{cob(I)alamin} \longrightarrow \text{THF} + \text{enzyme}\cdot\text{methylcobalamin} \quad (1)$$

$$\text{enzyme}\cdot\text{methylcobalamin} + \text{homocystine} \longrightarrow \text{enzyme}\cdot\text{cobalamin} + \text{methionine} \quad (2)$$

methyl corrinoids have been implicated in the biosynthesis of methane and acetate (5). Vitamin B_{12} itself has an essential role in metabolism in man and animals. Diets deficient in vitamin B_{12} often result in the development of anemia (6). The most recently discovered role of

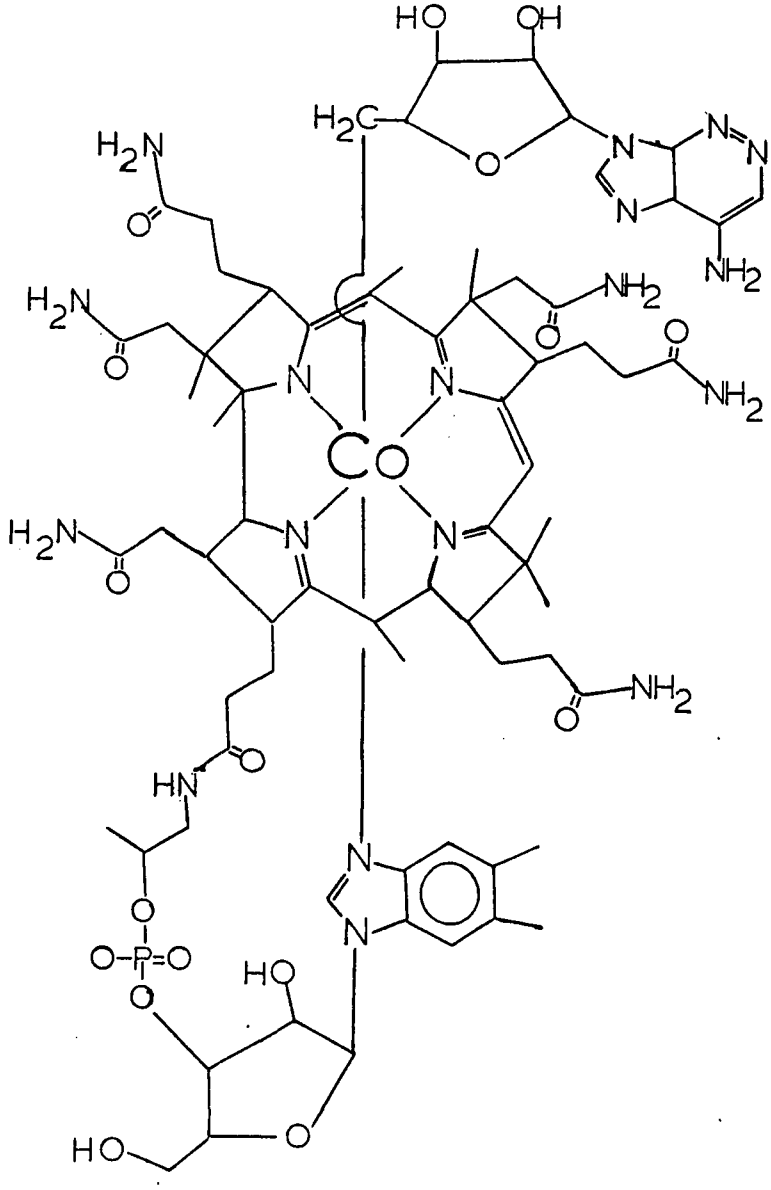


Figure 1. Structure of 5'-deoxyadenosylcobalamin.

vitamin B_{12} and alkylcobalamins is related to the area of trace metal pollution.

Many heavy metals are released into the environment in a relatively nontoxic form. They can acquire enhanced toxicity as organometals through interaction with various naturally occurring alkylating agents. It is believed that methylcorrinoid derivitives (i.e., methylcobalamin) are the methylating agents for inorganic salts since they are the only known methylating agents capable of transferring a methyl carbanion (CH_3^-) <u>in vivo</u>. Other methylating agents, such as S-adenosylmethionine and N^5-tetrahydrofolate, donate methyl carbocations (CH_3^+) and thus cannot effectively interact with the positively charged inorganic metals (7, 8, 9). These reactions can be exemplified best by the production of monomethyl- and dimethylmercury from the reaction of mercuric ion with methylcobalamin (methyl group replaces adenosyl moity in Figure 1) (10, 11, 12), the biomethylation of arsenic (13, 14), and the biotransformation of Pb^{2+} into $(CH_3)_4Pb$ (7, 15).

The realization that the corrin ring is an important factor in the stabilization of the cobalt-carbon bond led to interest in the preparation and study of organocobalt corrinoids and organocobalt complexes of analogous tetradentate ligands. The result has been an incredible volume of work; and the number of organocobalt complexes that have been reported is more than one thousand (16, 17).

What is particularly interesting about these synthetic organocobalt complexes is the similarity of their properties and reactivity with those of the naturally occurring organocobalt corrinoids. The similarity is not limited to the stable cobalt-carbon bond, but includes, for example, the reversible formation of oxygen adducts with cobalt(II) complexes and the relative stability of both the +1 and +4 oxidation states (18, 19).

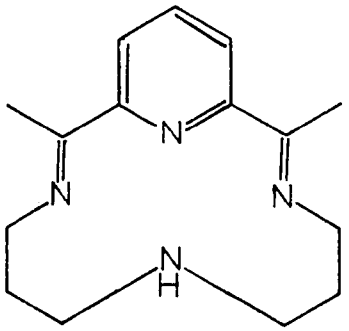
The synthetic organocobalt complexes can be characterized according to the number of alkyl or aryl groups bonded directly to cobalt. Both mono- and diorgano complexes are known. The chemistry of the well known monoorgano complexes has been reviewed in two rather lengthy articles (16, 17). The diorgano complexes are few in number, and their chemistry has received much less attention (20).

Preparation of Organocobalt Complexes

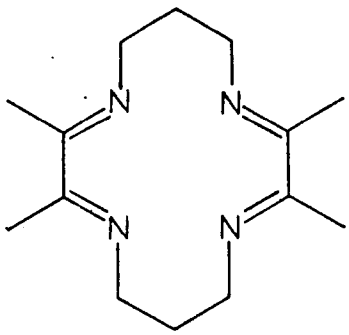
Figure 2 shows a variety of ligands[1] which have been used to prepare cobalt complexes that contain a stable cobalt-carbon bond. As can be seen by examining this figure, all the ligands will form 5- or 6-membered chelate

---

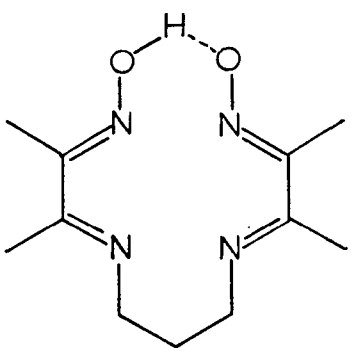
[1]Ligand abbreviations are based on conventions described by Melson (21). [14]tetraenato(2^-)N_4 = bis-(3,4-dimethylglyoximato(1^-)); [14]tetraenato(1^-)N_4 = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaunadeca-1,3,8,10-tetraen-11-ol-1-olato; Me_4[14]tetraeneN_4 = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; Me_2pyo[14]-trieneN_4 = 2,12-dimethyl-3,7,11,17-tetraazabicyclo (11·3·11)-heptadeca-1,(17),2,11,13,15-pentaene; [14]aneN_4 =



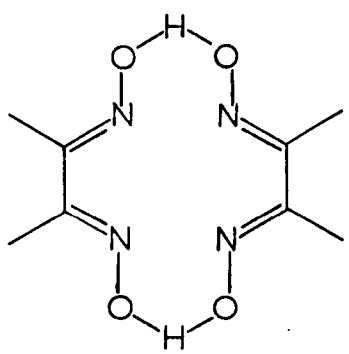
$Me_2pyo[14]trieneN_4$



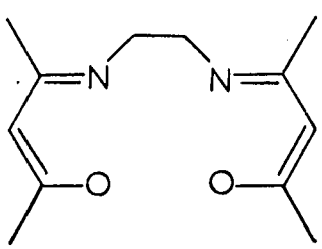
$Me_4[14]tetraeneN_4$



[14]tetraenato(1-)N_4

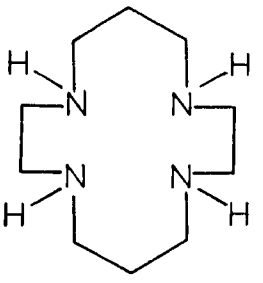


[14]tetraenato(2-)N_4

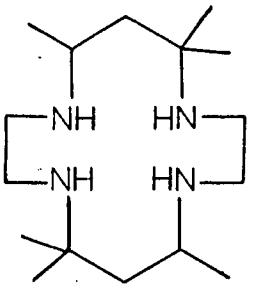


$acacen^{2-}$

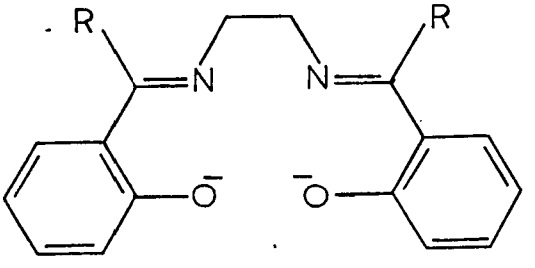
Figure 2. Structures of chelating ligands.



[14]aneN$_4$

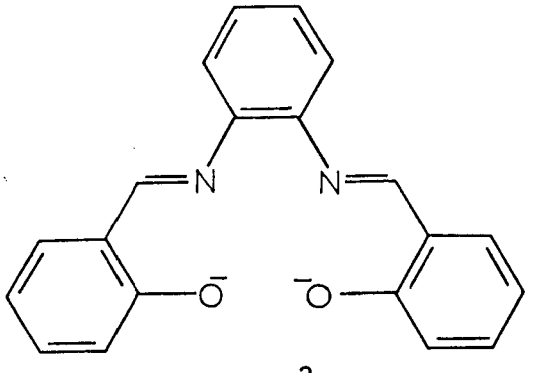


Me$_6$[14]aneN$_4$



salen^{2-} (R = H)

7,7'-(CH$_3$)$_2$salen (R = CH$_3$)



saloph^{2-}

Figure 2 - Continued.

rings upon complexation with cobalt, and the donor atoms are either all nitrogen (N_4) or nitrogen-oxygen (N_2O_2). Further examination indicates that most of the ligands listed are extensively unsaturated. It was believed that an unsaturated equatorial ligand was necessary to form stable cobalt-alkyl complexes (22, 23). This was presumably due to the need for a strong field ligand that could effectively π-bond to metal (24). The isolation of the methyl complexes of the saturated ligands [14]aneN$_4$ and Me_6[14]aneN$_4$ has since disproved this idea (25). Of the ligands listed in Figure 2, only Me_2pyo[14]triene N_4, Me_4[14]tetraeneN$_4$, and [14]tetraenato(1-)N_4 have been used in successful preparation of trans-dialkylcobalt complexes.

A review of the literature reveals that there are three methods used in the preparation of cobalt-carbon bonds. They are: (1) reaction of a carbanion with a cobalt(III) complex, (2) reaction of a carbon-centered radical with a cobalt(II) complex, and (3) reaction of a carbocation with a cobalt(I) complex. All three of these methods have been used to prepare monoalkylcobalt complexes, but only the first and third have been successfully used in the preparation of trans-dialkylcobalt complexes. These procedures will now be discussed individually.

1,4,8,11-tetraazacyclotetradecane; Me_6[14]aneN$_4$ = C-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; acacen^{2-} = N,N'-ethylene-bis(acetylacetone-iminato); salen^{2-} = bis(salicylaldehyde)-1,2-ethane; 7,7'-$(CH_3)_2$salen = N,N'-ethylene-bis(7,7'dimethyl-salicylideneiminato); saloph^{2-} = N,N'-O-phenylene bis(salicylideneiminato).

The reaction of a cobalt(III) complex with a carbanion source such as a Grignard or a lithium alkyl has been employed to prepare both mono- and diorganocobalt complexes (26, 27). The reactions are usually run at low temperature, and the ratio of RMgX to cobalt complex will determine whether the mono- or diorgano product is isolated. This method has been used to prepare $R_2Co([14]tetraenato-(1-)N_4)$ (R = CH_3, C_6H_5, and $C_6H_5CH_2$) only (eq 3 and 4).

$$Co([14]tetraenato(1-)N_4)Br_2 + CH_3MgX \xrightarrow[-60^{\circ}C]{THF} \xrightarrow{ClO_4^-} [CH_3Co([14]tetraenato(1-)N_4(H_2)]ClO_4 \quad (3)$$

$$Co([14]tetraenato(1-)N_4)Br_2 + 2CH_3MgX \xrightarrow[-60^{\circ}C]{THF} (CH_3)_2Co([14]tetraenato(1-)N_4) \quad (4)$$

No reports of the preparation of the corresponding Me_4[14]-tetraeneN_4 or Me_2pyo[14]trieneN_4 by this method have appeared, although the method would appear to be applicable.

The second general method used to prepare organocobalt complexes involves the reaction of a carbon-centered radical with a cobalt(II) complex, as shown in eq 5. This

$$R\cdot + Co^{II}(chel) \longrightarrow R\text{-}Co^{III}(chel) \quad (5)$$

procedure has found limited success and has been restricted to the preparation of monoorganocobalt complexes. The diorganocobalt complexes cannot be prepared by this route because of the instability of the intermediate

monoorganocobalt(II), which undergoes disproportionation (eq 6) (28). It is interesting to examine the methods

$$2RCo^{II}(chel) \longrightarrow R_2Co^{III}(chel) + Co^{I}(chel) \quad (6)$$

used to generate the radicals in these preparations. Goedkin and coworkers (29) and Dey and De (30) used the oxidative decomposition of organic hydrazines as their radical source:

$$R\text{-}NHNH_2 \longrightarrow R\cdot + N_2 \quad (7)$$

The reactions, catalyzed by transition metals, are nearly quantitative. Roche and Endicott (24) generated methyl radicals by the photolysis of carboxylatopentamminecobalt-(III) complexes in the presence of the appropriate Co^{II} complex (eq 8). Yields from this procedure, however, are

$$[Co(NH_3)_5O_2CR]^{2+} \xrightarrow[H^+]{h\nu} Co^{2+} + 5NH_4^+ + CO_2 + R\cdot \quad (8)$$

not as high as those obtained in the work with organic hydrazines (40%). Espenson and Martin (31) have used tert-alkyl hydroperoxides as their radical source. Again the yields do not match those obtained in the work with

$$R_3C\text{-}COOH + Co^{II}(chel) \longrightarrow R_3CO\cdot + Co^{III}(chel)OH \quad (9)$$

$$R_3C\text{-}O\cdot \longrightarrow R_2CO + R\cdot \quad (10)$$

$$R\cdot + Co^{II}(chel) \longrightarrow R\text{-}Co^{III}(chel) \quad (11)$$

organic hydrazines, but they do approach the theoretical 50% that is predicted on the basis of the scheme above (eq 9-11).

Method three, the most generally useful route for preparation of both mono- and diorganocobalt complexes, is the nucleophilic displacement reaction by Co^{I}(chel) with an alkyl halide (eq 12). It has been well established (32, 33) that the reaction between the very nucleophilic Co^{I}

$$Co^{I}(chel) + RX \longrightarrow R\text{-}Co^{III}(chel) + X^{-} \qquad (12)$$

(Pearson's nucleophilic reactivity constant, $\eta > 13$ (34)) and the alkyl halide proceeds by an S_N2 mechanism. The cobalt(I) complex is often generated in the presence of the alkyl halide by the use of sodium borohydride in a protic solvent such as methanol. Alternatively, the cobalt(I) species can be generated with sodium amalgam in an inert solvent such as acetonitrile. After removal of the excess amalgam the appropriate alkyl halide is added.

The formation of diorganocobalt complexes by this procedure implies that an intermediate species such as RCo^{I}(chel) must exist. The existence of such intermediates was proved by the preparation of unsymmetrical diorganocobalt complexes, RR'Co(chel). For example, as shown in eq 13 and 14, the preparation of methyl-phenyl derivatives by reduction of C_6H_5Co([14]tetraenato(1-)N_4)I by sodium amalgam in THF, followed by addition of methyl bromide, yielded the mixed diorgano product (35).

$$C_6H_5Co([14]tetraenato(1-)N_4)I + Na(Hg) \xrightarrow[N_2]{THF} [C_6H_5Co^{I}([14]tetraenato(1-)N_4)]^- \quad (13)$$

$$[C_6H_5Co^{I}([14]tetraenato(1-)N_4)]^- + CH_3Br \longrightarrow (C_6H_5)(CH_3)Co([14]tetraenato(1-)N_4) \quad (14)$$

During their synthesis of the trans-dialkylcobalt complexes [RR'Co(chel)]Y (R = R' = CH_3 or $C_6H_5CH_2$; R = CH_3, R' = $C_6H_5CH_2$; chel = Me_4[14]tetraeneN$_4$ or Me_2pyo[14]triene-N$_4$; Y = PF_6^-, $B(C_6H_5)_4^-$), Farmery and Busch (36) isolated the stable organocobalt(I) species $RCo^{I}(Me_4[14]tetraeneN_4)$ and $RCo^{I}(Me_2pyo[14]trieneN_4)$ (eq 15). By reaction with the appropriate alkyl halide, a rapid quantitative conversion to the corresponding diorganocobalt(III) complexes was achieved (eq 16). The importance of these preparations is that they confirm unambiguously that the postulated RCo^{I}-(chel) species do exist.

$$[CH_3Co^{III}(Me_4[14]tetraeneN_4)X]^+ + Na(Hg) \longrightarrow CH_3Co^{I}(Me_4[14]tetraeneN_4) \quad (15)$$

$$CH_3Co(Me_4[14]tetraeneN_4) + CH_3I \longrightarrow [(CH_3)_2Co(Me_4[14]tetraeneN_4)]^+ + I^- \quad (16)$$

Characterization

The crystal and molecular structures of $(CH_3)_2$Co-[14]tetraenato(1-)N$_4$, $[CH_3Co([14]tetraenato(1-)N_4(H_2O)]$-$ClO_4$, and $[(CH_3OOCCH_2)Co([14]tetraenato(2-)N_4)(pyridine)]$

(37, 38, 39) were determined by X-ray methods. In all three cases the four nitrogen atoms of the macrocyclic ligand occupy the equatorial positions and all are coplanar. The cobalt atom is displaced only 0.02 - 0.05 Å from the plane defined by the nitrogen atoms. In the two [14]tetraenato-(1-)N_4 complexes the six-membered ring has the expected flattened chair configuration. The short C-C (1.45 Å) and the N-C (1.30 Å) bond lengths in the two five-membered rings are indicative of extensive delocalization. These bond lengths agree with the mean C-C (1.46 Å) and N-C (1.28 Å) bond lengths in the [14]tetraenato(2-)N_4 complex.

The cobalt-carbon bond lengths in $(CH_3)_2$Co([14]tetraenato(1-)N_4) are equal and have a mean value of 2.047 Å. This is similar to the cobalt-carbon bond length in coenzyme B_{12} (2.05 Å) and the [14]tetraenato(2-)N_4 complex (2.04 Å); and it is slightly longer than the bond length in the corresponding monomethyl complex (1.99 Å). The N-Co-C bond angles in all three complexes are very close to 90°, which indicates a nearly perpendicular orientation of the coordinated organic moiety with respect to the macrocycle.

^1H and ^{19}F NMR have been used to characterize both mono- and diorganocobalt complexes. Table 1 lists the shift values for several CH_3Co(chel)X complexes. The high field position of the methyl resonances, common for organo groups bound to cobalt, is due to the build up of charge

TABLE 1

NMR SHIFT VALUES FOR MONO- AND DIORGANOCOBALT COMPLEXES

Complex	Co-CH_3[a]	Solvent	Reference
$(CH_3)_2Co(Me_2pyo[14]trieneN_4)$	0.18	$(CD_3)_2SO$	36
$CH_3Co([14]tetraenato(1-)N_4)X$			
X = CH_3	0.06	$CDCl_3$	40
C_6H_5	0.35	$CDCl_3$	40
p-FC_6H_4	.36	$CDCl_3$	40
m-FC_6H_4	.38	$CDCl_3$	40
I	.71	$CDCl_3$	40
H_2O	.83	$(CD_3)_2SO$	41
$[CH_3Co(Me_4[14]tetraeneN_4)Y]^{n+}$			
Y = CH_3	.35	CD_3CN	36
CH_3CN	1.30	CD_3CN	42
I	1.15	$(CD_3)_2SO$	42

[a] ppm vs. TMS

density on cobalt which is caused, in part, by the electron-donating ability of the methyl group (43, 44). This effect is demonstrated in the series of complexes, CH_3Co([14]-tetraenato(1-)N_4)X (X = CH_3, C_6H_5, p-FC_6H_4, m-FC_6H_4, I, H_2O) and $[CH_3Co(Me_4[14]tetraeneN_4)Y]^{n+}$ (Y = CH_3, CH_3CN, I) (Table 1), where the axial methyl chemical shift increases in the order, for X, H_2O < I < m-FC_6H_4 < p-FC_6H_4 < C_6H_5 < CH_3, and for Y, I < CH_3CN < CH_3. This result is in good agreement with a study of the <u>trans</u>-effect in [p-FC_6H_4Co-([14]tetraenato(1-)N_4)X] by ^{19}F NMR (45) which also showed the superior σ-donor strength of the methyl group (CH_3 > m-FC_6H_4 > OCN^- > Br^- > SCN^- > I).

The use of infrared spectroscopy for characterization of macrocyclic organocobalt complexes has been limited. The <u>trans</u>-effect was studied in a series of [CH_3Co([14]-tetraenato(1-)N_4)X] complexes (46) (X = $(C_6H_5)_3P$, C_5H_5N, $(CH_3)_2S$, H_2O). It was found that as the donor strength of the ligand in the <u>trans</u>-position increased, ν(Co-CH_3) shifted to higher frequency. The assignments of (Co-CH_3) (488 cm^{-1}) and (Co-CD_3) (467 cm^{-1}) by Witman and Weber (47) are in agreement with the above-mentioned study and are consistent with the σ-donor strength of the methyl group.

Reactions

Generally, reactions of RCo(chel)X and R_2Co(chel) occur with cleavage of the cobalt-carbon bond or with

substitution of X. These dealkylation reactions can be classified as being homolytic or heterolytic in nature. The homolytic reaction will yield a carbon-centered radical intermediate (eq 17). In a heterolytic reaction, the organocobalt complex can yield either a carbanion (eq 18) or carbocation (eq 19) depending upon the nature of the attacking species. These reactions will be discussed individually with respect to both mono- and diorganocobalt complexes.

$$RCo^{III}(chel) \longrightarrow Co^{II}(chel) + R\cdot \qquad (17)$$

$$RCo^{III}(chel) \longrightarrow Co^{III}(chel) + R:^{-} \qquad (18)$$

$$RCo^{III}(chel) \longrightarrow Co^{I}(chel) + R^{+} \qquad (19)$$

Homolytic Bond Cleavage: Radical Reactions

Homolytic bond cleavage often occurs in both types of cobalt complexes upon exposure to light or upon pyrolysis (eq 20 and 21) (48, 49). The radical species can abstract a hydrogen atom (RH) or dimerize (RR) to form an alkene or lose a hydrogen atom to form an alkene (eq 22). The

$$RCo^{III}(chel) \xrightarrow[N_2]{h\nu \text{ or } \Delta} Co^{II}(chel) + R\cdot \qquad (20)$$

$$RCo^{III}(chel) \xrightarrow[N_2]{h\nu \text{ or } \Delta} Co^{I}(chel) + 2R\cdot \qquad (21)$$

$$R\cdot \longrightarrow RH, RR, \ldots \qquad (22)$$

cobalt(I) or cobalt(II) species are observed only if the reaction is carried out anaerobically. In the presence of oxygen, oxidation of the reduced cobalt species occurs to produce a cobalt(III) complex.

Only monoorganocobalt complexes undergo reactions where the organo group leaves as a radical. These reactions are typified by the methylation of Cr^{2+} and Sn^{3+} by methylcobalamin (eq 23) (50, 51), the alkylation of Cr^{2+} by [RCo([14]tetraenato(2-)N_4)(H_2O)] (R = CH_3, C_2H_5, n-C_3H_7, $C_6H_5CH_2$, etc.) (eq 24) (52), and the alkylation of [Co^{II}-(chel)(H_2O)$_2$] by [RCo^{III}(chel)(H_2O)] (R = CH_3, C_6H_5) (53).

$$CH_3B_{12} + Cr^{2+} \xrightarrow{H^+/H_2O} [CH_3Cr(H_2O)_5]^{2+} + B_{12r} \quad (23)$$

$$[RCo([14]tetraenato(2-)N_4)_2(H_2O)] + Cr^{2+} \xrightarrow{H^+/H_2O} [CH_3Cr(H_2O)_5]^{2+} + Co^{2+} + 2H_2[14]tetraenato(2-)N_4 \quad (24)$$

The kinetic data for these reactions is indicative of a bimolecular mechanism, and the thermodynamics of the reaction are consistent with a radical transfer occurring in the transition state.

Nucleophilic Reactions

Carbocation Donation

Reactions in which an organo group is transferred from a cobalt complex as a carbocation (R^+) are also limited to the monoorgano complexes. These reactions can

be viewed as a nucleophilic attack on the α-carbon of the alkyl group. The displacement of a very nucleophilic cobalt(I) complex causes the reaction to be reversible if Co^{I}(chel) is a comparable nucleophile to Nu: (eq 25).

$$Nu: + RCo(chel) \rightleftharpoons NuR + Co^{I}(chel) \qquad (25)$$

The reversibility of the reaction is also dependent on the presence of substances, such as oxygen, which can remove the Co^{I}(chel) as it is produced.

Another point which clouds the picture with respect to nucleophilic attack of organocobalt complexes is that it is not always obvious whether the nucleophile attacks at the alkyl group or elsewhere in the molecule. Examples of this include the reaction of RCo(salen) with CN^{-} and $C_2H_5S^{-}$ (48), and [RCo([14]tetraenato(1-)N_4)(H_2O)]$^{+}$ with CN^{-}, $C_6H_5S^{-}$, and HS^{-} (54). In the former case (eq 26 and 27) the nucleophile coordinates <u>trans</u> to the alkyl group and causes dealkylation to occur. In the latter case (eq 28) nucleophilic attack by CN^{-} occurs at the position

$$RCo(salen) + CN^{-} \xrightarrow{fast} [RCo(salen)(CN)]^{-} \qquad (26)$$

$$[RCo(salen)(CN)]^{-} \xrightarrow[CN^{-}]{slow} [Co(salen)(CN)_2]^{-} + R^{-} \qquad (27)$$

$$[RCo([14]tetraenato(1-)N_4)(H_2O)]^{+} + CN^{-} \xrightarrow{fast} [RCo([14]tetraenato(1-)N_4)(CN)] + H_2O \qquad (28)$$

trans to the alkyl group, but in this case there is no dealkylation. Thus, a great deal of ambiguity exists in the literature concerning the mechanism of dealkylation of organocobalt complexes by nucleophiles.

Electrophilic Reactions: Carbanion Donation

Electrophilic reactions which cleave the cobalt-carbon bond in both mono- and diorganocobalt complexes include halogens, protonic acids, and a variety of metallic electrophiles. Reactions of the monoorganocobalt complexes have been studied in more detail (16, 17) and will be summarized first. The electrophilic reactions of the diorganocobalt complexes will be discussed later.

Complexes of the type [RCo(chel)X], where chel = [14]tetraenato(2-)N_4, salen, acacen, [14]tetraenato(1-)N_4, and X = H_2O or pyridine, are readily dealkylated by halogens in what was first thought to be an electrophilic cleavage (S_E2) of the cobalt-carbon bond (55). This conclusion was based on the results of kinetic studies that showed rate data consistent with an S_E2 process. Surprisingly, the reaction also proceeded with inversion of configuration at the α-carbon of the alkyl group (eq 29).

$$\underline{\text{cis}}\text{-4-bromocyclohexylpyridinatocobaloxime} + Br_2 \xrightarrow[-5^{\circ}C]{CH_2Cl_2} \underline{\text{trans}}\text{-dibromocyclohexane} + \text{BrCo([14]tetraenato(2-)}N_4)_2\text{py} \qquad (29)$$

This was explained in terms of the cobalt-carbon bond being very hindered to front-side attack in alkylcobalamins. A short time later it was reported that [RCo([14]tetraenato-(2-)N_4)$_2$(H_2O)] was susceptible to oxidation by $IrCl_6^{2-}$ (eq 30), and that the oxidized organocobalt was susceptible to nucleophilic attack by halide (eq 31). The configuration of the alkyl halide product was the same as that found

$$[RCo([14]tetraenato(2-)N_4)(H_2O)] + IrCl_6^{2-} \longrightarrow [RCo^{IV}([14]tetraenato(2-)N_4)(H_2O)]^+ + IrCl_6^{3-} \quad (30)$$

$$[RCo([14]tetraenato(2-)N_4)(H_2O)]^+ + Cl^- \longrightarrow RCl + [Co([14]tetraenato(2-)N_4)(H_2O)_2]^+ \quad (31)$$

with electrophilic attack. Abley et al. suggested (57) that the same products could be obtained by a radical decomposition of the oxidized organocobalt complex. The evidence exists that more than one mechanism is in effect in these electrophilic displacement reactions, and it is not obvious which one is predominant.

Monoorganocobalt complexes are not dealkylated by H_3O^+, nor are they dealkylated by several metallic electrophiles such as Pb^{2+}, Cd^{2+}, In^{3+}, Tl^+, etc. (16, 58). These complexes are readily dealkylated by Hg^{2+}, Tl^{3+}, Pt^{4+}/Pt^{2+}, and Au^{3+}/Au^+ (58). The mechanism of the dealkylation of [RCo(chel)X] by Hg^{2+} is probably the most extensively studied electrophilic transfer reaction (9, 10, 57-61). Interest in this reaction is presumably due to

the potential role of CH_3B_{12} in the formation of CH_3Hg^{2+}. The reaction has been demonstrated to be second order overall (eq 32), first order with respect to Hg^{2+} and RCo(chel).

$$RCo(chel) + Hg^{2+} \longrightarrow Co(chel)^{+} + RHg^{+} \qquad (32)$$

The reaction has been described as proceeding by an S_E2 mechanism with the surprising result that inversion occurs at the α-carbon of the transferred R group (62, 63). Dealkylation of [RCo(chel)X] by Tl^{3+} is similar to the dealkylation of Hg^{2+} discussed above, except that no organothallium compounds are isolated. In the presence of chloride the sole product is chloromethane (eq 33).

$$[RCo(chel)X] + Tl^{3+} \longrightarrow [MeTl^{2+}] \xrightarrow{Cl^-} MeCl + Tl^{+} \qquad (33)$$

An interesting mechanism has been postulated for the demethylation of methylcobalamin (CH_3B_{12}) by Pt^{IV} and Au^{III} (58, 64). Methylcobalamin is not demethylated by Pt^{IV}, Pt^{II}, Au^{III}, or Au^{I} alone, but is completely demethylated by a mixture of either Pt^{IV}-Pt^{II} or Au^{III}-Au^{I}. The reaction stoichiometry is shown in eq 34. Kinetic

$$CH_3B_{12} + Pt^{IV} + H_2O \xrightarrow{Pt^{II}} B_{12a} + CH_3Pt^{IV} \qquad (34)$$

data along with information from ^1H NMR studies suggest two possible mechanisms. In both cases it is assumed that Pt^{II} coordinates to the CH_3B_{12} to form a CH_3B_{12}-Pt^{II} complex. The coordination site is not known but is thought

to be in the amide side chains of the A and D rings of the corrin. The first pathway is a two-electron "redox switch" between Pt^{II} and Pt^{IV} (eq 35). The second pathway (eq 36)

$$CH_3\text{-}B_{12}\text{-}Pt^{II} + {}^*Pt^{IV} + H_2O \longrightarrow B_{12a} + CH_3\text{-}Pt^{IV} + {}^*Pt^{II} \quad (35)$$

$$CH_3\text{-}B_{12}\text{-}Pt^{II} + Pt^{IV} + H_2O \longrightarrow B_{12a} + CH_3Pt^{IV} + Pt^{II} \quad (36)$$

is a direct electrophilic attack by Pt^{IV} on the cobalt-carbon bond in the CH_3B_{12}-Pt^{II} complex. The role of the Pt^{II} would be to labilize the cobalt-carbon bond to electrophilic attack by Pt^{IV}. It is assumed that the mechanism of the Au^{III}/Au^{I} reaction is similar.

One last example of carbanion transfer in monoorganocobalt complexes involves the electrophilic attack of $[Co^{III}(chel)(H_2O)_2]^+$ on the methyl group of $[CH_3Co(chel)(H_2O)]$ (53, 65). What is of interest here is that the methyl donor and acceptor properties of the complexes are determined by the equatorial ligands. The general reaction scheme is shown in eq 37 and 38. Costa et al. found that the complexes studied could be arranged in the following order, such that the methylating power decreased from

$$[CH_3Co(chel)(H_2O)] + [Co(chel^*)(H_2O)_2]^+ \xrightarrow[RT]{H_2O/MeOH} [Co(chel)(H_2O)_2]^+ + [CH_3Co(chel^*)(H_2O)] \quad (37)$$

$$[CH_3Co(chel)(H_2O)] + [Co([14]tetraenato(1-)N_4)-(H_2O)]^{2+} \xrightarrow[RT]{H_2O/MeOH} [Co(chel)(H_2O)_2]^+ + [CH_3Co([14]tetraenato(1-)N_4)(H_2O)]^+ \quad (38)$$

left to right: chel = bae > $(CH_3)_2$salen > salen > saloph > cobalamin > ([14]tetraenato(2-)$N_4)_2$ > ([14]tetraenato-(1-)N_4) (i.e., CH_3Co(salen) will methylate saloph but not $(CH_3)_2$salen). The order parallels the order of polarographic half-wave potentials for the reduction of Co^{III}-(chel) to Co^{II}(chel) (19, 66). This is indicative of an increase in ligand donor power, and hence an increase in effective charge on the cobalt in going from [14]tetraenato(1-)N_4 to bae. Thus methyl transfer will occur from the less electrophilic complex to the more electrophilic one.

The reactions of diorganocobalt complexes, in contrast to monoorgano complexes, are limited to those in which the complex can act as a carbanion donor. There have been no reports of reactions involving a macrocyclic diorganocobalt complex acting as a carbocation donor or radical donor. The distinct difference in reactivity is a manifestation of the increased electron density on cobalt that arises because of the presence of a second organo group, which is a strong σ-donor, in the <u>trans</u> position. This results in the cobalt-carbon bond being very polarized. The alkyl (aryl) group will always be cleaved as a carbanion. The

inability of [$(CH_3)_2$Co([14]tetraenato(1-)N_4)] to methylate $[Co^{II}(chel)(H_2O)_2]^+$ (53) is a demonstration of this fact (eq 39). For reaction to occur, the methyl group would have to be transferred as a radical.

$$(CH_3)_2Co([14]tetraenato(1-)N_4) + [Co^{II}(chel)(H_2O)_2]^+ \longrightarrow \text{No reaction} \quad (39)$$

Reactions of the dimethylcobalt complexes have not been studied to the extent that the corresponding monomethyl complexes have been. The reaction of $R^1R^2Co([14]$-tetraenato(1-)N_4) ($R^1 = R^2 = CH_3$, C_6H_5; $R^1 = CH_3 \neq R^2 = C_6H_5$) with halogens was studied (67). Dreos et al. found that the reaction showed two different stoichiometries, depending on the molar ratios of the reactants (eq 40 and 41). When ICl was used as the attacking reagent, they

$$R_2Co([14]tetraenato(1-)N_4) + I_2 \xrightarrow[RT]{} RCo([14]tetraenato(1-)N_4)I + RI \quad (40)$$

$$R_2Co([14]tetraenato(1-)N_4) + 2I_2 \xrightarrow[RT]{} Co([14]tetraenato(1-)N_4)I_2 + 2RI \quad (41)$$

found that RI was the sole organic product (eq 42). No RCl was produced. Another finding was that when the

$$R_2Co([14]tetraenato(1-)N_4) + ICl \longrightarrow RCo([14]tetraenato(1-)N_4)Cl + RI \quad (42)$$

unsymmetrical cobalt complex $R(C_6H_5)Co([14]tetraenato(1-)-N_4)$, where R = CH_3, C_2H_5, was the reactant, the aliphatic carbon was more readily cleaved (eq 43).

$$R(C_6H_5)Co([14]tetraenato(1-)N_4) + I_2 \longrightarrow C_6H_5Co([14]tetraenato(1-)N_4)I + RI \quad (43)$$

In contrast to the monomethylcobalt complexes which are not dealkylated by H_3O^+, the dialkyl complexes are readily decomposed by acid to the corresponding monomethyl complex and methane (eq 44) (68, 69). Titration data

$$R_2Co(chel) + H_3O^+ \longrightarrow RCo(chel) + CH_4 \quad (44)$$

indicates that the reaction occurs with the expected 1:1 stoichiometry, and kinetic studies under pseudo first-order conditions (excess H_3O^+) show a first-order dependence on the concentration of the dimethylcobalt complex. The calculated second-order rate constants are greater for $(CH_3)_2Co([14]tetraenato(1-)N_4)$ than for $(CH_3)_2Co(Me_4[14]-tetraeneN_4)^+$. This difference in rate constants reflects the electrostatic repulsion between the positively charged $Me_4[14]tetraeneN_4$ species and H_3O^+, as opposed to the neutral $[14]tetraenato(1-)N_4$ species with H_3O^+.

Reactions of dimethylcobalt complexes with diaquocobalt complexes have been studied by several groups (53, 68, 70). It has been found that these reactions occur as shown in eq 45 (where chel = $[14]tetraenato(1-)N_4$ or

$$(CH_3)_2Co(chel) + Co(chel')(H_2O)_2^+ \longrightarrow$$
$$CH_3Co(chel)(H_2O)^+ + CH_3Co(chel')(H_2O) \quad (45)$$

Me_4[14]tetraeneN_4; chel' = salen, saloph, Me_2salen). The reactions occur with the indicated 1:1 stoichiometry and proceed to completion. When the diaquo complex of [14]-tetraenato(1-)N_4 or [14]tetraenato(2-)N_4 is used as the electrophile, no reaction occurs. The only observable reaction is slow evolution of methane which presumably arises from the reaction of the dimethyl complex and H_3O^+ that is added to repress the acid dissociation of the diaquo complexes. Espenson et al. suggested (68) that these transmethylation reactions are probably controlled by the substitution rate for the diaquocobalt complexes. Although not proven, this conclusion is logical because the second-order rate constants for these methyl transfers are virtually identical for both the Me_4[14]tetraeneN_4 and [14]tetraenato(1-)N_4 complexes.

The alkylation of Hg^{2+} and $C_6H_5Hg^+$ by $R_2Co(chel)$ (chel = [14]tetraenato(1-)N_4, Me_4[14]tetraeneN_4, Me_2pyo-[14]trieneN_4) has been reported (68, 71). The reactions of phenylmercuric ion with the diorganocobalt complexes occur very rapidly (eq 46). In fact, when R = C_2H_5, n-C_3H_7, C_6H_5, the reaction proved too rapid for stopped-flow

$$R_2Co(chel) + C_6H_5Hg^+ \longrightarrow$$
$$RCo(chel)(H_2O) + C_6H_5HgR \quad (46)$$

techniques (second-order rate constant > 10^7 L-m^{-1}-s^{-1}). The reactions of $(CH_3)_2Co([14]tetraenato(1-)N_4)$ with Hg^{2+} show a two-step mechanism corresponding to the transfer of both methyl groups to mercury (eq 47 and 48). When the

$$(CH_3)_2Co([14]tetraenato(1-)N_4) + Hg^{2+} \xrightarrow{fast} [CH_3Co([14]tetraenato(1-)N_4)(sol)]^+ + CH_3Hg^+ \quad (47)$$

$$[CH_3Co([14]tetraenato(1-)N_4)(sol)]^+ + Hg^{2+} \xrightarrow{slow} [Co([14]tetraenato(1-)N_4)(sol)_2]^{2+} + CH_3Hg^+ \quad (48)$$

reaction is run with the dimethyl complex in excess, a third reaction is observed (eq 49), corresponding to the formation of dimethylmercury.

$$CH_3Co([14]tetraenato(1-)N_4) + CH_3Hg^+ \longrightarrow [CH_3Co([14]tetraenato(1-)N_4)(sol)]^+ + (CH_3)_2Hg \quad (49)$$

The reaction of Ag^+ and $(CH_3)_2Co(chel)$ was first reported by Costa and coworkers (70). They found that the reaction yielded a silver mirror, with ethane as the predominant organic product (eq 50). A free radical mechanism

$$(CH_3)_2Co(chel) + Ag^+ \longrightarrow CH_3Co(chel)^+ + Ag^0 + C_2H_6 + CH_4 \quad (50)$$

had been proposed to account for the formation of ethane. This idea has been disputed and more detailed work indicates that simple dimerization of methyl radicals to yield ethane is not the predominant pathway. A more reasonable

explanation is intermolecular reductive elimination of the CH_3Ag (eq 51).

$$2CH_3Ag \longrightarrow Ag^0 + C_2H_6 \qquad (51)$$

The reactivity and kinetics of the reaction of $(CH_3)_2Co([14]tetraenato(1-)N_4)$ with Zn^{2+}, Cd^{2+}, and Pb^{2+} were studied by Witman and Weber (72). These reactions showed two different stoichiometries, depending on whether the complex or the metal ion was in excess. When the metal ion was in excess the reaction described in eq 52 occurred. The CH_3M^+ products slowly decomposed by reacting with $i\text{-}C_3H_7OH$ solvent. The reactions with the complex in excess proceeded as described by eq 52 and 53. The very

$$(CH_3)_2Co([14]tetraenato(1-)N_4) + M^{2+} \xrightarrow{fast} [CH_3Co([14]tetraenato(1-)N_4]^+ + CH_3M^+ \qquad (52)$$

$$(CH_3)_2Co([14]tetraenato(1-)N_4) + CH_3M^+ \xrightarrow{slow} [CH_3Co([14]tetraenato(1-)N_4)]^+ + (CH_3)_2M \qquad (53)$$

reactive $(CH_3)_2M$ was decomposed by reaction with $i\text{-}C_3H_7OH$ to produce methane and the metal isopropoxide.

$$CH_3M^+ + i\text{-}C_3H_7OH \longrightarrow CH_4 + M(i\text{-}C_3H_7O)^+ \qquad (54)$$

$$(CH_3)_2M + 2i\text{-}C_3H_7OH \longrightarrow 2CH_4 + M(i\text{-}C_3H_7O)_2 \qquad (55)$$

II. EXPERIMENTAL

General Methods

All reactions between the dimethyl complexes and electrophiles were performed in the dark under an atmosphere of pre-purified nitrogen. ^{1}H-NMR spectra were recorded on a Varian EM360 NMR spectrometer. ^{207}Pb and ^{1}H temperature-dependent NMR were recorded on a Jeol FX-90Q FT NMR spectrometer. The proton decoupled ^{207}Pb spectra were obtained with sweep width of 20 kHz, a sweep frequency of 46.33 kHz (obs) and an irradiating frequency of 54.2 kHz. The ^{1}H spectra were obtained with a sweep width of 750 Hz and a sweep frequency of 44.55 kHz (obs). Acetonitrile-d_3 (CD_3CN) was the source of an internal deuterium lock. EPR spectra (0-5000 gauss) were recorded on a Varian E-4 X-band spectrometer operated at a microwave frequency of 9.089 GHz, a modulation amplitude of 0.63 x 10^{1} G, and a microwave power output of 5 mW. Electronic spectra in the 200-700 nm range were recorded on a Cary Model 14 or 219 recording spectrophotometer. A Varian Aerograph series 1860-1 chromatograph equipped with a flame ionization detector and a 6' x 1/8" OV-17 (3% on chromsorb-W, 80-100 mesh) maintained at 60^{o}C or a 6' x 1/8" porapak Q (80-100 mesh) column maintained at 115^{o}C was used to determine volatile reaction products. X-ray powder diffraction patterns were determined with a North

American Philips X-ray generator using Ni-filtered Cu K_α radiation. Infrared spectra (IR) were recorded on a Perkin-Elmer Model 283B infrared spectrophotometer. Solution scattering experiments were done with a Perkin-Elmer Model 204 spectrofluorometer and a Perkin-Elmer 150 Xenon lamp supply. Metal ion concentrations were determined by atomic absorption spectrometry with a Techtron AA5 spectrometer. Elemental analyses (C,H,N) were performed on a Perkin-Elmer Model 240B elemental analyzer or an F and M Model 185 CHN analyzer by Mrs. Deana Cardin.

Materials

1. 2,3-Butanedione was purchased from Aldrich Chemical Company and was distilled before use
2. 1,3-Diaminopropane and methyl iodide were purchased from Eastman and were distilled before use
3. 2,3-Butanedione monoxime was purchased from Eastman and was used as received
4. $CoBr \cdot 4H_2O$ and $NaBH_4$ (pellets) were purchased from Ventron and were used as received
5. $Co(CH_3COO)_2 \cdot 4H_2O$, $NaB(C_6H_5)_4$, and Nitron were purchased from J. T. Baker and were used as received
6. $Pb(ClO_4)_2 \cdot 3H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, $Cd(ClO_4)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $Cr(ClO_4)_3 \cdot 6H_2O$, and $LiClO_4 \cdot 3H_2O$ were purchased from G. F. Smith Chemical Company and were recrystallized from water before use

7. $NaClO_4 \cdot H_2O$ was purchased from Apache Chemicals and was used as received
8. Cl_2 gas was purchased from Union Carbide Corporation and was used as received
9. $(CH_3)_4Pb$ (80% solution w/w in toluene) was a gift of the Ethyl Corporation and was used as received
10. Acetonitrile was purchased from J. T. Baker and was purified by the method of Coetzee (73) before use
11. 2-Propanol was purchased from J. T. Baker and was purified by the method of Wiberg (74) and then distilled under N_2 before use
12. Ag_2O was prepared in quantitative yield by the reaction of NaOH with $AgNO_3$ in CO_2-free water (75)
13. $AgNO_3$ was prepared in quantitative yield by the reaction of HNO_3 with Ag metal. Large crystals of $AgNO_3$ were obtained by evaporation of the excess acid and water (assayed at 99.999% pure by Mohr titration)
14. Acetonitrile-d_3 was purchased from Stohler Isotopes and was used as received
15. Hypo-vials (10, 50, 125 mL) were purchased from Pierce Chemical Company
16. Rubber serum caps were purchased from A. H. Thomas Company

All other solvents used were purchased from commercial sources and were purified by standard methods (76) before use. All other reagents used were purchased from commercial sources and were used as received.

Standardization of Stock Metal Solutions

For Spectral Titrations

Solutions of $Pb(ClO_4)_2 \cdot 3H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$ and $Cd(ClO_4)_2 \cdot 6H_2O$ were prepared in acetonitrile. The solutions were standardized by complexometric titration with EDTA as the primary standard (77). Analytical grade $Na_2H_2EDTA \cdot 2H_2O$ was dried at 95°C for 3 h, and then 29.84760 g (0.080184 mol) was dissolved in 500.00 mL of water at 20.0°C. The resulting concentration was 0.16037 M.

The Pb^{2+} solution was pipetted into an Erlenmeyer flask and a spatula-tip of tartaric acid was added. Five milliliters of pH 10 buffer was added and the solution was diluted to 75 mL with distilled-deionized water. The Erio T indicator was added and the solution titrated with EDTA until the color changed from violet to clear blue. The procedure was repeated to yield a final concentration of 0.2342 M.

The Zn^{2+} and Cd^{2+} solutions were titrated in a similar manner except that the tartaric acid was omitted. The final concentrations of the Zn^{2+} and Cd^{2+} solutions were 0.2624 and 0.2027 M, respectively.

The Cu^{2+} solution was standardized in a manner similar to that used for Zn^{2+} and Cd^{2+} except that murexide was used as the end-point indicator. The final concentration of the Cu^{2+} solution was 0.2174 M.

The Cr^{3+} solution was standardized by atomic absorption spectrometry. A 50-μL aliquot of the stock Cr^{3+} solution was diluted to 250 mL with acidic distilled-deionized water. The solution's atomic absorbance was compared to a standard curve and the concentration of the stock Cr^{3+} solution was calculated to be 0.536 M.

Standard solutions of $(CH_3)_2Pb(NO_3)_2$ and $(CH_3)_3PbCl$ were prepared by dissolving known quantities of analytically pure samples of the organolead salts in volumetric flasks of appropriate volume at 20.0°C. Because of the known decomposition of organolead salts in solution (78, 79), only small volumes (2 mL) were made at any time and were stored in the freezer.

For NMR Titrations

A solution of $Pb(ClO_4)_2 \cdot 3H_2O$ was made in CD_3CN. A 35-μL aliquot of the Pb^{2+} solution was diluted to 500 mL with acidic distilled-deionized water. The Pb^{2+} concentration was then determined by atomic absorption spectrometry. The concentration of the stock Pb^{2+} solution was then calculated to be 0.142 M.

Solutions of $Zn(ClO_4)_2 \cdot 6H_2O$ and $Cd(ClO_4)_2 \cdot 6H_2O$ were made in CD_3CN and standardized in the same manner as that used for $Pb(ClO_4)_2$. The final concentrations of the Zn^{2+} and Cd^{2+} solutions were 0.272 and 0.203 M, respectively.

Determination of Lead in $(CH_3)_2Pb(NO_3)_2$ and $(CH_3)_3PbCl$

Fifty-milligram samples of the organolead salts were decomposed in a 20 x 150 mm test tube by treatment with 2 mL of 1:1 sulfuric:nitric acid solution. The solution was then evaporated to dryness with a Bunsen burner. The procedure was repeated if the residue was not pure white in color. The residue ($PbSO_4$) was dissolved in 3 mL of 1:2 glacial acetic acid:aqueous ammonia and quantitatively transferred to a 250-mL Erlenmeyer flask. The resulting solution was diluted to 75 mL with water; a spatula-tip of tartaric acid was added, and the solution was buffered at pH = 10 with an ammonia/ammonium chloride buffer. The solution was titrated with 0.01604 M EDTA to an Eriochrome T end point. The procedure was repeated to yield 71.85% Pb in $(CH_3)_2PbCl$ (Calcd: 72.01%) and 57.48% Pb in $(CH_3)_2Pb(NO_3)_2$ (Calcd: 57.34%).

Gravimetric Analysis of NO_3^- in $(CH_3)_2Pb(NO_3)_2$ (81)

Five-hundred-milligram samples of $(CH_3)_2Pb(NO_3)_2$ were dissolved in 75 mL of water to which 1 mL of glacial acetic acid had been added. The solution was heated nearly to boiling and then 15 mL of nitron reagent (5.0 g nitron in 50 mL 5% acetic acid) was added. The solution was cooled at 0°C for 2.5 h. The precipitate was collected in a tared crucible, washed successively with 15 mL of a cold, saturated

nitron nitrate solution and 6 mL of cold water. The crucible was dried to constant weight at 105°C. The solid was weighed as $C_{20}H_{16}N_4 \cdot HNO_3$. The analysis was repeated to yield an average value of 34.70% nitrate (Calcd: 34.35%).

Co([14]tetraenato(1-)N_4)Br_2 (47, 82)

A solution of butanedione monoxime (30.00 g, 0.30 mol) and 1,3-diaminopropane (11.10 g, 0.15 mol) in 400 mL of benzene was magnetically stirred at reflux for 3 h. Water from the reaction was removed with a Dean-Stark trap. The reaction mixture was poured into a 500-mL separatory funnel and the product (ligand), ([14]tetraenato(1-)N_4), separated as a thick brown oil. The oil was drawn off and dissolved in 400 mL of acetone, to which $CoBr_2 \cdot 4H_2O$ (60.0 g, 0.20 mol) in 100 mL of water was added. The solution was stirred and aerated overnight. The deep-green, crystalline solid that precipitated was collected on a glass frit, washed with cold water, cold acetone, and diethyl ether and dried under vacuum. The yield based on $CoBr_2 \cdot 4H_2O$ was 29.4% (26.90 g). Anal. Calcd for $C_{11}H_{19}N_4O_2CoBr_2$: C, 28.84; H, 4.15; N, 12.23%. Found: C, 28.84; H, 4.26; N, 12.38%.

[Co([14]tetraenato(1-)N_4)-$(H_2O)_2$]$(ClO_4)_2$ (69)

Co([14]tetraenato(1-)N_4)Br_2 (4.69 g, 10.25 mmol) was dissolved in 100 mL of acetone. An aqueous solution of

$AgNO_3$ (3.76 g, 22.0 mmol) was added. The solution was heated and stirred for 30 min to digest the precipitated silver bromide. The solution was cooled in an ice-water bath and then filtered through celite. The filtrate was placed in an evaporating dish and an aqueous solution of $NaClO_4 \cdot H_2O$ (14.0 g, 102 mmol) was added. The acetone was air evaporated and, after 48 h, the dark brown crystals were collected by filtration. The yield, based on Co([14]tetraenato(1-)N_4)Br_2, was 63% (3.35 g). Anal. Calcd for $C_{11}H_{23}N_4O_{12}CoCl_2$: C, 24.77; H, 4.32; N, 10.51%. Found: C, 24.10; H, 3.99; N, 9.50%.

[Co([14]tetraenato(1-)N_4)$(H_2O)_2$]$(NO_3)_2$

The same procedure used for the preparation of [Co([14]tetraenato(1-)N_4)$(H_2O)_2$]$(ClO_4)_2$ was employed except that no $NaClO_4 \cdot H_2O$ was added to the filtrate prior to the evaporation of the acetone. The yield was 60% based on Co([14]tetraenato(1-)N_4)Br_2. Anal. Calcd for $C_{11}H_{23}N_6O_{10}Co$: C, 28.83; H, 5.02; N, 18.34%. Found: C, 28.42; H, 5.08; N, 17.95%.

$(CH_3)_2$Co([14]tetraenato(1-)N_4) (47)

The dimethyl complex was prepared from either [Co([14]tetraenato(1-)N_4)$(H_2O)_2$]$(ClO_4)_2$ or [Co([14]tetraenato(1-)N_4)$(H_2O)_2$]$(NO_3)_2$ as the starting material.

[Co([14]tetraenato(1-)N_4)$(H_2O)_2$]$(ClO_4)_2$ (5.3 g, 10.0 mmol) was dissolved in 100 mL of methanol in a 600-mL

beaker. The beaker was placed in an ice-water bath and surrounded with a black cloth. Four milliliters of 5 M sodium hydroxide (20 mmol) was added dropwise, followed by the addition of 12 mL of methyl iodide (200 mmol). The slow addition of aqueous $NaBH_4$ (1.00 g, 26.4 mmol) resulted in a bright orange solution. The solution was stirred an additional 5 min during which time a vigorous effervescence occurred and the bright orange crystals of the product precipitated. The product was collected by filtration and was washed with cold water. The $(CH_3)_2Co$([14]tetraenato-(1-)N_4) was recrystallized from acetone by the addition of water. The yield, based on [Co([14]tetraenato(1-)N_4)-$(H_2O)_2](ClO_4)_2$, was 77% (2.52 g). Anal. Calcd for $C_{12}H_{25}N_4O_2Co$: C, 47.57; H, 7.62; N, 17.07%. Found: C, 47.53; H, 7.79; N, 17.16%.

$[Co(Me_4[14]tetraeneN_4)Cl_2]ClO_4$ (83)

Reagent HCl (19.7 g, 0.20 mol) was slowly added to a solution of 1,3-diaminopropane (15.0 g, 0.20 mol) in 600 mL of degassed methanol. 2,3-Butanedione (17.2 g, 0.20 mol) was added from a dropping funnel over a period of 25 min. Then $Co(CH_3COO)_2 \cdot 4H_2O$ (24.9 g, 0.10 mol) was added and the solution was stirred under N_2 for 3.5 h. Then 65 mL reagent HCl was added and the solution was aerated over a period of 20 h. At this point 100 mL of 70% $HClO_4$ was added and the solution was cooled in an ice bath. The grey-green crystals that separated were collected, washed

with cold 10% HCl (methanol) and air dried. The yield, based on $Co(CH_3COO)_2 \cdot 4H_2O$, was 10% (4.7 g). Anal. Calcd for $C_{14}H_{24}N_4O_4Cl_3Co$: C, 35.20; H, 5.03; N, 11.73%. Found: C, 35.08; H, 5.13; N, 11.74%. UV-VIS (rel. abs.): 575 nm (0.04), 430 nm (0.15), 395 nm (1.0).

$[Co(Me_4[14]tetraeneN_4)Br_2]Br$ (84)

Forty-eight percent HBr (32.6 g, 0.20 mol) was slowly added to a solution of 1,3-diaminopropane (15.0 g, 0.20 mol) in 600 mL of degassed methanol. From a dropping funnel 2,3-butanedione (17.2 g, 0.20 mol) was added to the solution over a period of 25 min. Then $Co(CH_3COO)_2 \cdot 4H_2O$ (24.9 g, 0.10 mol) was added and the solution stirred under N_2. After 3 h, 70 mL of 48% HBr was added, the solution was aerated for 3.5 h and filtered. A green powder was collected, washed with 5% HBr (methanol) and air dried. The product was recrystallized from hot aqueous 5% HBr to yield dark green crystals. The yield, based on $Co(CH_3COO)_2 \cdot 4H_2O$, was 22% (11.82 g). UV-VIS (rel. abs.): 300 nm (8.0), 393 nm (1.0), 595 nm (0.03).

$[Co(Me_4[14]tetraeneN_4)Br_2]ClO_4$ (83)

$[Co(Me_4[14]tetraeneN_4)Br_2]Br$ (6.90 g, 12.6 mmol) was dissolved in 100 mL of aqueous methanol (1:4). With cooling 70% $HClO_4$ was added dropwise, whereupon a light green crystalline solid precipitated. The product was collected on a frit, washed with cold methanol and dried under

vacuum. The yield, based on the bromide, was 98% (7.0 g). UV-VIS (rel. abs.): 306 nm (8.0), 390 nm (1.0), 595 nm (0.03). Anal. Calcd for $C_{14}H_{24}N_4O_4Br_2ClCo$: C, 29.67; H, 4.24; N, 9.89%. Found: C, 29.62; H, 4.29; N, 9.88%.

$$\underline{[Co(Me_4[14]tetraeneN_4)-(H_2O)_2](ClO_4)_2 \quad (31)}$$

Over a 25-min period, 70% $HClO_4$ (57.8 g, 0.40 mol) was added to a solution of 1,3-diaminopropane (30.0 g, 0.40 mol) in 700 mL of degassed methanol. To the resulting solution, 2,3-butanedione (34.4 g, 0.40 mol) was added over a 20-min period. Then $Co(CH_3COO)_2 \cdot 4H_2O$ (49.8 g, 0.20 mol) was added and the solution was stirred under nitrogen. After 4 h, 20 mL of deoxygenated water and 50 mL of 70% $HClO_4$ were added and the methanol was partially evaporated by a vigorous nitrogen purge. After 6 h, the mixture was filtered under nitrogen and the deep purple crystalline product was collected, washed with dry ether and dried under vacuum. The yield, based on $Co(CH_3COO)_2 \cdot 4H_2O$, was 12.5% (13.61 g). Anal. Calcd for $C_{14}H_{28}N_4O_8Cl_2Co$: C, 31.00; H, 5.17; N, 10.33%. Found: C, 31.38; H, 5.06; N, 10.40%.

$$\underline{[Co(Me_4[14]tetraeneN_4)-(H_2O)_2](ClO_4)_3}$$

$[Co(Me_4[14]tetraeneN_4)Br_2]ClO_4$ (2.00 g, 3.53 mmol) was suspended in 150 mL of acetone. An aqueous solution

of $AgNO_3$ (1.20 g, 7.07 mmol) was added. The solution was heated and stirred for 1 h. During this time the solution slowly changed color from green to purple as the silver bromide precipitated. The mixture was then cooled in an ice bath and filtered through celite. The filtrate was placed in an evaporating dish, and an aqueous solution of $NaClO_4 \cdot H_2O$ (7.40 g, 52.9 mmol) was added. The acetone was air evaporated. After 48 h the brown crystals were collected by filtration and air dried. The yield, based on $[Co(Me_4[14]tetraeneN_4)Br_2]ClO_4$, was 81.7% (1.85 g).

$$\underline{[CH_3Co(Me_4[14]tetraeneN_4)(CH_3CN)]-(B\emptyset_4)_2 \cdot CH_3CN \ (85)}$$

$[Co(Me_4[14]tetraeneN_4)(H_2O)_2](ClO_4)_2$ (3.00 g, 5.52 mmol) was dissolved in 900 mL of degassed 1:1 $CH_3OH:CH_3CN$. Methyl iodide (57.0 g, 400 mmol) was added to the solution. Then, with vigorous stirring, $NaBH_4$ (0.222 g, 5.52 mmol) was added. The solution was stirred for several minutes and then filtered in air. $NaB(C_6H_5)_4$ (14.0 g, 41 mmol) in a minimum amount of methanol was added to the filtrate. The solution volume was reduced on a rotary evaporator to 300 mL. The solution was cooled in ice, and the golden crystals that separated were collected on a glass frit, washed with ether and dried. The product was recrystallized from acetonitrile by the addition of ether. The yield, based on $[Co(Me_4[14]tetraeneN_4)(H_2O)_2](ClO_4)_2$, was 76.3% (4.39 g). Anal. Calcd for $C_{67}H_{73}N_6B_2Co$: C,

77.20; H, 7.01; N, 8.06%. Found: C, 77.23; H, 7.12; N, 8.18%.

$[(CH_3)_2Co(Me_4[14]tetraeneN_4)]-B(C_6H_5)_4\cdot CH_3OH$

$[Co(Me_4[14]tetraeneN_4)(H_2O)_2](ClO_4)_2$ (2.00 g, 3.60 mmol) was dissolved in 600 mL of methanol under a nitrogen atmosphere. Fifty percent sodium hydroxide was added dropwise until the solution turned deep blue. Then $NaBH_4$ (0.0725 g, 1.92 mmol) was added with vigorous stirring, followed immediately by the addition of methyl iodide (22 mL, 353 mmol). The solution was stirred under nitrogen for 5 min. During this time it slowly took on an orange color. Then a second portion of $NaBH_4$ (0.142 g, 3.75 mmol) was added. The solution slowly took on a deep red color. The clear solution was then filtered in air and $NaB(C_6H_5)_4$ (5.00 g, 14.6 mmol) in methanol was added. The filtrate was cooled in an ice bath and the bright red solid that separated was collected and dried under a vacuum. The yield, based on $[Co(Me_4[14]tetraeneN_4)(H_2O)_2](ClO_4)_2$, was 91% (2.19 g). Anal. Calcd for $C_{41}H_{54}N_4BOCo$: C, 71.5; H, 7.85; N, 8.14%. Found: C, 71.1; H, 7.73; N, 8.15%.

$[(CH_3)_2Co(Me_4[14]tetraeneN_4)]ClO_4 \cdot (H_2O)$

From $[Co(Me_4[14]tetraeneN_4)Cl_2]ClO_4$

$[Co(Me_4[14]tetraeneN_4)Cl_2]ClO_4$ (1.50 g, 3.14 mmol) was dissolved in 200 mL of 1:1 methanol:acetonitrile. Ten milliliters of methyl iodide (0.16 mol) was added, followed by the dropwise addition of a basic methanol solution of $NaBH_4$ (0.475 g, 12.6 mmol). The solution slowly turned bright red with effervescence. After 30 min $NaClO_4$ (2.20 g, 15.7 mmol) was added and the solution was concentrated on the rotary evaporator. The bright red crystals that separated were collected, washed with cold methanol, and dried under vacuum. The yield, based on $[Co(Me_4[14]tetraeneN_4)Cl_2]ClO_4$, was 35% (0.50 g). Anal. Calcd for $C_{16}H_{30}N_4O_4ClCo$: C, 44.00; H, 6.88; N, 12.83%. Found: C, 43.27; H, 6.88; N, 12.76%.

From $[Co(Me_4[14]tetraeneN_4)(H_2O)_2](ClO_4)_3 \cdot 2H_2O$

$[Co(Me_4[14]tetraeneN_4)(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ (1.04 g, 1.5 mmol) was dissolved in 20 mL of methanol in a 200-mL beaker. Five molar sodium hydroxide (0.6 mL, 3 mmol) was added dropwise with stirring. The beaker was surrounded with a black cloth and then 2.5 mL of methyl iodide (5.7 g, 40 mmol) was added. The solution was cooled in an ice bath and aqueous $NaBH_4$ (0.1575 g, 4.2 mmol) was added with vigorous stirring. The solution was stirred an additional

10 min and then concentrated under vacuum. The bright red mixture was filtered and the product was collected, washed with ether and dried under vacuum. The yield, based on the diaquo starting material, was 60% (0.41 g). Anal. Calcd for $C_{16}H_{32}N_4O_5CoCl$: C, 42.26; H, 7.04; N, 12.33%. Found: C, 42.50; H, 6.97; N, 12.50%.

$(CH_3)_3PbCl$ (86)

Hydrogen chloride, generated from the reaction of NaCl with concentrated H_2SO_4, was used to saturate 75 mL of dry diethyl ether at 0°C. Tetramethyllead (6 mL of the 80% solution in toluene, 7.60 g, 28.0 mmol) was slowly added with stirring. The solution was stirred an additional 25 min at 0°C, during which time a white solid precipitated. The flask was removed from the ice bath and allowed to reach room temperature. The product was collected by filtration, washed with several portions of dry diethyl ether, and dried under vacuum. The yield based on $(CH_3)_4Pb$ was 92% (7.34 g). Anal. Calcd for C_3H_9PbCl: C, 12.52; H, 3.13; Pb, 72.01%. Found: C, 12.64; H, 3.15; Pb, 72.85%.

$(CH_3)_2PbCl_2$ (87, 88)

Tetramethyllead (6.3 mL of the 80% solution in toluene, 8.0 g, 30 mmol) was dissolved in 75 mL of ethyl acetate at -20°C. Chlorine gas was bubbled through the solution until the chlorine color persisted and the reaction

mixture had warmed to -8°C. The solution was stirred an additional 30 min while it slowly warmed to +2°C. The mixture was filtered and the white solid that had precipitated was collected and washed with several portions of cold ethyl acetate. The crude product was recrystallized from warm (T < 40°C) DMF. The yield based on $(CH_3)_4Pb$ was 93% (8.60 g). Anal. Calcd for $C_2H_6PbCl_2$: C, 7.79; H, 1.95. Found: C, 7.84; H, 1.93.

$(CH_3)_2PbO$ (88)

$(CH_3)_2PbCl_2$ (3.00 g, 9.70 mmol) was dissolved in a minimum amount of water. Excess Ag_2O (5.0 g, 21.6 mmol) was added and the mixture was stirred for 45 min. The precipitated AgCl and excess Ag_2O were removed by filtration, and the $(CH_3)_2Pb(OH)_2$ was precipitated from the filtrate by the addition of acetone. The product was washed with acetone and diethyl ether. The $(CH_3)_2Pb(OH)_2$ was dehydrated by vacuum drying over P_2O_5. The yield based on the dichloride starting material was 92% (2.26 g).

$(CH_3)_2Pb(NO_3)_2$ (89)

$(CH_3)_2PbO$ (1.035 g, 4.26 mmol) was dissolved in 20 mL of water to which 540 µL (8.52 mmol) reagent nitric acid had been added. The solution was stirred several minutes and then the water was removed under vacuum with very gentle heating. The product was collected and dried under vacuum. The yield based on $(CH_3)_2PbO$ was 99% (1.53 g).

Anal. Calcd for $C_2H_6PbN_2O_6$: C, 6.65; H, 1.66; N, 7.76; Pb, 57.34; NO_3^-, 34.35%. Found: C, 6.66; H, 1.66; N, 6.02; Pb, 57.48; NO_3^-, 34.65%.

Determination of the Molar Absorptivities

The molar absorptivities of the two dimethyl complexes used in this study were determined in acetonitrile. This was done by preparing standard solutions of the complexes in the dark under nitrogen, transferring an aliquot of the solution to an anaerobic 1-cm quartz cell, and recording the solution's electronic spectrum from 700-200 nm. A matched 1-cm quartz cell containing acetonitrile was used as a reference. The molar absorptivity at 442 nm for $[(CH_3)_2Co(Me_4[14]tetraeneN_4)]ClO_4$ and 410 nm for $[CH_3Co(Me_4[14]tetraeneN_4)(CH_3CN)](ClO_4)_2$ were obtained from the least-squares slope of the Beer's law plot shown in Figure 3. The molar absorptivity at 405 nm for $(CH_3)_2Co([14]tetraenato(1-)N_4)$ and 390 nm for $[CH_3Co([14]tetraenato(1-)N_4)(CH_3CN)]ClO_4$ were obtained from the least-squares slope of the Beer's law plot shown in Figure 4. The molar absorptivity values are found in Table 3 in the Results and Discussion Section.

Spectrophotometric Titrations

Typically 1 x 10^{-4} M solutions of the dimethyl complexes were made up in 125-mL serum vials. 2.80 mL aliquots of the solutions were transferred via syringe to an

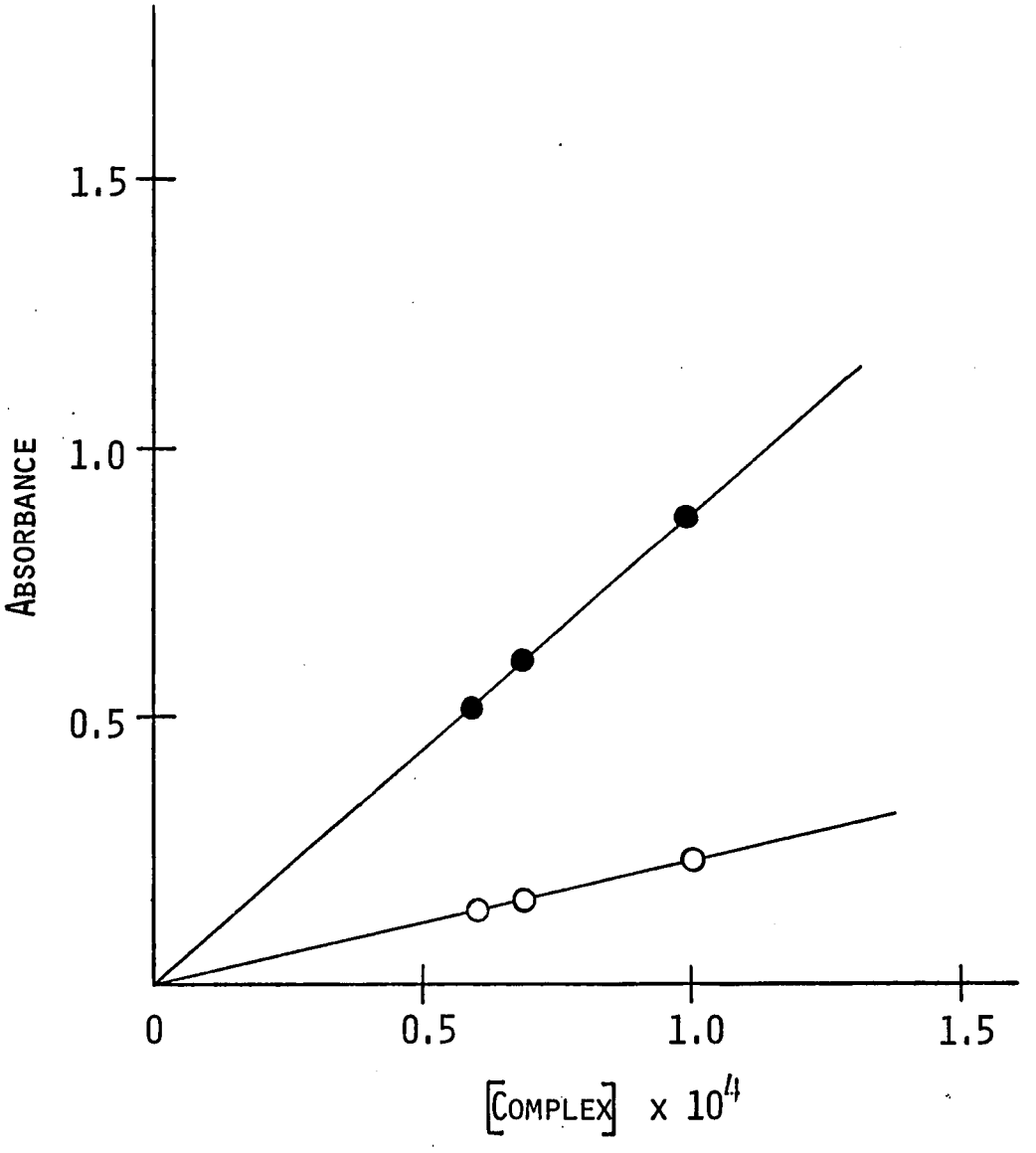


Figure 3. Beer's law plot for the determination of the molar absorptivity value of $[(CH_3)_2Co([14]tetraeneN_4)]ClO_4$ at 442 nm (●) and $[CH_3Co(Me_4[14]tetraeneN_4)(CH_3CN)]ClO_4$ at 410 nm (○).

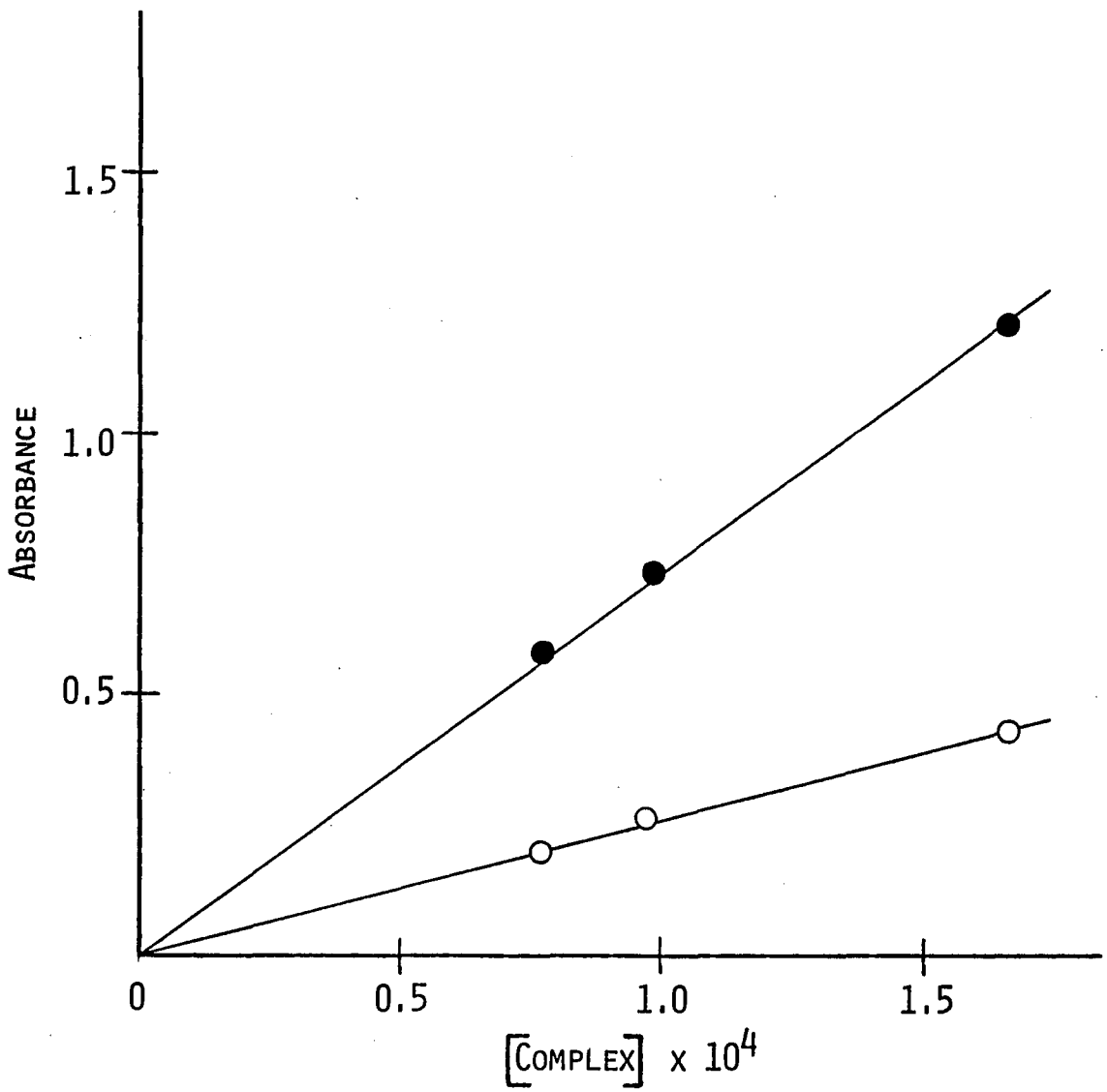


Figure 4. Beer's law plot for the determination of the molar absorptivity value of $(CH_3)_2Co([14]tetraenato(1-)N_4)$ at 405 nm (●) and $[CH_3Co([14]tetraenato(1-)N_4)(CH_3CN)]ClO_4$ at 390 nm (○).

anaerobic 1-cm quartz cell. The solutions were titrated with the various electrophiles, and progress of the reaction was monitored by observing the decrease in the absorbance due to the dimethyl complexes (λ_{max} = 445 nm, ε = 8630 cm^{-1}-$\underline{M}^{-1}$ for (Me_4[14]tetraeneN_4); λ_{max} = 405 nm, ε = 7222 cm^{-1}-$\underline{M}^{-1}$ for ([14]tetraenato(1-)N_4)). The titrant additions were made from a 1-μL syringe, and the solution was allowed to achieve equilibrium between additions. Attempts were made to titrate the fast first reaction by adding small volumes of the electrophile from a 1-μL syringe, mixing the solution, recording the solution absorbance, and repeating the process as rapidly as possible. Mixing times were on the order of 5-10 s by this procedure, and the titration was complete within a few minutes.

Gas Chromatographic Analysis of Volatile Reaction Products

Anaerobic solutions of the dimethyl complexes were made up in 50-mL hypo-vials that were sealed with rubber serum caps. The reactions were initiated by the addition of the appropriate electrophile from a syringe. The atmosphere over the reaction mixture was monitored by GLC. The identities of the volatile reaction products were determined by retention time comparison (see Table 2) and peak height enhancement with known standards. The quantity of volatile reaction products produced was determined by the method of standard additions.

TABLE 2

GLC CONDITIONS AND RETENTION TIMES

Compound	Conditions	Retention Time
methane	OV-17, 60°C	66 s
	Porapak-Q, 115°C	30 s
tetramethyllead	OV-17, 60°C	128 s
ethane	Porapak-Q, 115°C	54 s
acetonitrile	OV-17, 60°C	90 s
	Porapak-Q, 115°C	21.5 min

NMR Titrations

Typically 0.030 M solutions of the dimethyl complexes were made up anaerobically in acetonitrile-d_3. One-half-milliliter aliquots of the solutions were transferred with a syringe to an anaerobic 5-mm NMR tube. The solutions' NMR spectra were recorded, and then the solutions were titrated with the various electrophiles. The progress of the reactions were monitored by observing changes in the solutions' NMR spectra.

Low temperature NMR studies were done using the Jeol FX-90Q FT NMR spectrometer. The cavity temperature was maintained at -35°C and the titrant solutions were cooled to -40°C by means of a dry ice-o-xylene-m-xylene slush before addition. The titrations were performed as outlined above.

Nephelometric Titration

A 1×10^{-4} M solution of $(CH_3)_2Co(chel)$ in acetonitrile was titrated with small aliquots (1-2 μL) of 0.2201 M Pb^{2+}. Changes in the solution scattering were monitored with addition of Pb^{2+}, by irradiating the solution at 500 nm and analyzing at 500 nm. Two blank titrations were performed as well. First the Pb^{2+} solution was titrated into neat acetonitrile; and second, neat acetonitrile was titrated into a solution of the dimethyl complex. These measurements were made with the same instrument parameters listed above.

Attempted Identification of the Precipitate from the Reaction of $[(CH_3)_2Co(chel)]$ with Excess Pb^{2+}

$[(CH_3)_2Co(Me_4[14]tetraeneN_4)]ClO_4 \cdot H_2O$ (14.99 mg, 0.330 mmol) was dissolved in 5.00 mL of acetonitrile in a hypo-vial. The vial was purged with nitrogen and then 600 µL of a 0.2201 M Pb^{2+} solution was added. The reaction was allowed to proceed to completion. The solution was then filtered through a 0.40 µm polycarbonate membrane by use of a glass support. The bright yellow solid was mounted on a glass capillary and its X-ray powder diffraction pattern was obtained by Ni filtered Cu K_α radiation (λ = 1.545 Å). A KBr pellet of the yellow solid was made and its infrared spectrum was taken. Under the same reaction conditions $(CH_3)_2Co([14]tetraenato(1-)N_4)$ did not yield a precipitate.

Identification of the Precipitate from the Reaction of Pb^{2+} with Excess $[(CH_3)_2Co(chel)]$

$[(CH_3)_2Co(Me_4[14]tetraeneN_4)]ClO_4 \cdot H_2O$ (13.67 mg, 0.301 mmol) was dissolved in 5.00 mL of acetonitrile in a hypo-vial. The vial was sealed and purged with nitrogen; then 34 µL of a 0.2201 M Pb^{2+} solution was added. The reaction was allowed to proceed to completion. At that time the solution was filtered through a 0.40 µm polycarbonate membrane by use of a glass support. The black solid

collected was washed with acetonitrile and air dried. The solid was mounted on a glass capillary and its X-ray diffraction pattern was obtained by Ni-filtered Cu K_α radiation (λ = 1.545 Å) and 2-h exposure time.

Under the same conditions, the reaction of $(CH_3)_2Co([14]tetraenato(1-)N_4)$ with Pb^{2+} yielded a black solid. Its X-ray powder diffraction pattern was determined as outlined above. Both solids were identified as lead metal on the basis of their X-ray powder diffraction patterns.

EPR Titrations: $[(CH_3)_2Co(Me_4[14]tetraeneN_4)]ClO_4$ with Pb^{2+}

A 600-μL aliquot of an anaerobic 2 x 10^{-2} M solution of $[(CH_3)_2Co(Me_4[14]tetraeneN_4)]ClO_4$ in acetonitrile was transferred via syringe to an anaerobic quartz EPR tube (3 mm i.d.). The EPR spectrum of the frozen solution (77K) was recorded prior to the initiation of the reaction. The quartz tube was warmed to room temperature and 50 μL of 0.2342 M Pb^{2+} was added. The reaction mixture was frozen and its EPR spectrum was monitored for change. The EPR tube was again warmed to room temperature, then refrozen, and its EPR spectrum was recorded. This freeze/thaw cycle was repeated several times, with the EPR spectrum of the frozen solution being recorded each time. Nitrogen bubbling was minimized by the method of Chasteen (90).

III. RESULTS AND DISCUSSION[2]

Synthesis

The complex $(CH_3)_2Co((1\text{-})N_4)$ (see Appendix) was prepared from both $[Co((1\text{-})N_4)(H_2O)_2](ClO_4)_2$ and $[Co((1\text{-})N_4)(H_2O)](NO_3)_2$ in high yield by the method of Witman (69). The use of the nitrate salt was found to be preferable because it eliminated the need to use a perchlorate salt which, although no such problems were encountered in this research, does tend to be explosive.

All aspects of the synthetic work with the (N_4) ligand system proved to be much more difficult than with the $((1\text{-})N_4)$ system. First attempts to prepare the complexes $[Co(N_4)X_2]^+$ ($X = Cl^-$, Br^-) by literature procedures (83) resulted in either very small yields (about 1-2%) or no product at all. Reported yields are in excess of 30% (83, 84). The reason for the low yields can only be speculated upon.

In addition to Co^{III}, the Ni^{II} (91) and Fe^{II} (92) complexes of (N_4) have been prepared and in each case the yield of the macrocyclic product is quite sensitive to a number of factors. These include hydrogen ion concentration, order and timing of reagent additions, and

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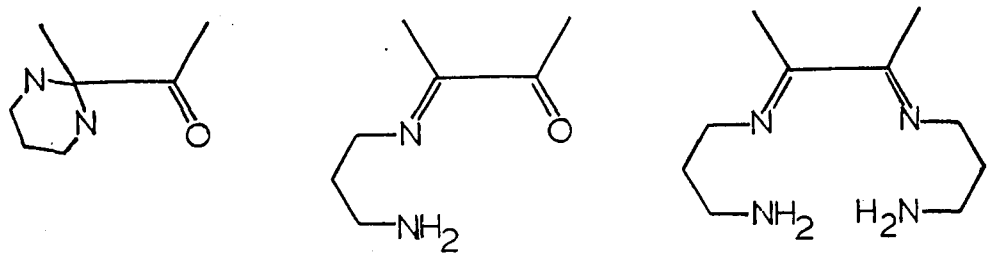
[2]In this section chel will be used to represent both macrocyclic ligands in general discussion. For specific examples the abbreviations (N_4) for $(Me_4[14]tetraeneN_4)$ and $((1\text{-})N_4)$ for ([14]tetraenato(1-)N_4) will be used.

temperature. From these requirements, Jackels and co-workers (83, 93) postulated that either some organic intermediate such as one of those shown below or the macrocycle itself is formed prior to the addition of the metal



ion. The conditions for the preparation of these complexes found in the Experimental Section have been optimized for maximum yield.

$[(CH_3)_2Co(N_4)]^+$ proved even more difficult to synthesize than the dihalide complexes just discussed. The reason for this difficulty is unclear but is most likely related to the reactivity of the $Co^I(N_4)$ species generated during the synthesis of $[(CH_3)_2Co(N_4)]^+$. Because the rate of reaction between $Co^I(N_4)$ and alkyl halides is very slow relative to other Co^I species, it often undergoes internal reductive decomposition or reacts with other potential electrophiles present in the reaction mixture to generate nonalkylated products (31, 94, 95). The deep blue color of Co^I(chel)X is discharged to the reddish-orange color of

$[CH_3Co^{III}(chel)X]^+$ by addition of methyl iodide for both (N_4) and $((1\text{-})N_4)$ complexes. The reaction occurs much faster for the $((1\text{-})N_4)$ complex.

The method of Farmery and Busch (36) was the first synthetic procedure tried. It involved the reduction of a monomethyl complex, $[CH_3Co(N_4)X]^+$, with either $NaBH_4$ in methanol or Na(Hg) in acetonitrile to yield a stable Co^I species, $CH_3Co(N_4)$ (eq 56). The addition of methyl iodide was expected to result in the rapid oxidative addition of $CH_3Co^I(N_4)$ to $[(CH_3)_2Co(N_4)]^+$ (eq 57).

$$[CH_3Co(N_4)X]^+ \xrightarrow{NaBH_4 \text{ or } Na(Hg)} CH_3Co^I(N_4) \qquad (56)$$

$$CH_3Co(N_4) + CH_3^+ \longrightarrow [(CH_3)_2Co(N_4)]^+ \qquad (57)$$

When this procedure was tried, work-up of the reaction mixture resulted in the isolation of a complex mixture consisting of $[CH_3Co(N_4)X]^+$, $[Co(N_4)X_2]^+$, and very small quantities, if any at all, of $[(CH_3)_2Co(N_4)]^+$.

The first success in obtaining $[(CH_3)_2Co(N_4)]^+$ was achieved by starting with the Co^{II} complex, $[Co(N_4)(H_2O)_2](ClO_4)_2$. The diaquocobalt(II) species is unstable with respect to disproportionation in basic solution, a fact used to advantage in the synthetic procedure. Since dissolution of the Co^{II} complex in an alkaline solution resulted in half of the cobalt being reduced to Co^I (eq 58), only half as much reducing agent was needed to reduce the remainder of the cobalt present. This is advantageous

$$2[Co^{II}(N_4)]^{2+} \xrightarrow{pH > 7} [Co^{I}(N_4)]^{+} + [Co^{III}(N_4)]^{3+} \quad (58)$$

because common reducing agents, such as $NaBH_4$, can readily reduce the imine functional groups present in the (N_4) macrocycle (42, 95). The $[Co^{I}(N_4)]^{+}$ was alkylated in the usual manner with methyl iodide, the monomethyl species was reduced once more, in situ, and realkylated to yield the final product. The dimethyl complex from this procedure (eq 59-62) was isolated as the tetraphenylborate salt in very high yield (about 91%).

$$2[Co(N_4)(H_2O)_2](ClO_4)_2 \xrightarrow{pH > 7} [Co^{I}(N_4)X]^{+} + [Co^{III}(N_4)X_2]^{3+} \quad (59)$$

$$[Co^{III}(N_4)]^{3+} \xrightarrow{NaBH_4} [Co^{I}(N_4)X]^{+} \quad (60)$$

$$2[Co^{I}(N_4)X]^{+} \xrightarrow{CH_3I} 2[CH_3Co(N_4)X]^{2+} \quad (61)$$

$$2[CH_3Co(N_4)X]^{2+} \xrightarrow{CH_3I/NaBH_4} 2[(CH_3)_2Co(N_4)]^{+} \quad (62)$$

Because of the expected lower solubility of the tetraphenylborate salt, it was concluded that the perchlorate salt of the dimethyl complex would be desirable. Instead of a crystalline perchlorate product, however, this procedure (eq 59-62) yielded an intractable, viscous, red oil. All attempts to crystallize the oil by stripping off the solvent under vacuum, drying in a vacuum desiccator,

and even repeated dissolutions in a variety of solvents failed.

The complex $[(CH_3)_2Co(N_4)]ClO_4$ was finally isolated as a monohydrate in moderate yield (about 60%) by using $[Co(N_4)(H_2O)_2](ClO_4)_3$ as the starting material. The synthetic procedure (eq 63) was an adaptation of one used by Witman (69) to prepare $(CH_3)_2Co((1\text{-})N_4)$. The dimethyl

$$[Co(N_4)(H_2O)_2](ClO_4)_3 \xrightarrow[OH^-/CH_3OH]{CH_3I} \xrightarrow[0^oC]{NaBH_4} [(CH_3)_2Co(N_4)]ClO_4 \qquad (63)$$

complex can also be prepared directly from $Co(N_4)Cl_2\ ClO_4$ by a similar procedure. The yields, however, were much lower (about 30-35%), presumably because of the strong competition between Cl^- and CH_3^- for the cobalt center.

Characterization

The dimethyl complexes used in this study were characterized by their electronic, IR, and ^{1}H-NMR spectra.

Electronic Spectra

The electronic spectra of the dimethyl complexes, $[(CH_3)_2Co(N_4)]ClO_4$ and $(CH_3)_2Co((1\text{-})N_4)$, were recorded in acetonitrile; the molar absorptivities of the corresponding monomethyl complexes and several other complexes were also determined (Table 3).

TABLE 3

ELECTRONIC ABSORPTION SPECTRA FOR COMPLEXES

Complex	Solvent	Wavelength (nm)[a]
$[(CH_3)_2Co(N_4)]ClO_4$	CH_3CN	442 (8630), 290[b] sh[c], 252 (19400)
$[CH_3Co(N_4)(CH_3CN)](ClO_4)_2$	CH_3CN	448 (2000) sh, 408 (2400), 310[b], 252 (4720)
$(CH_3)_2Co((1\text{-})N_4)$	CH_3CN	405 (7220), 276 (13000) sh, 236 (19600)
$[CH_3Co((1\text{-})N_4)(CH_3CN)]ClO_4$	CH_3CN	425 (1740) sh, 384 (2510), 320[b] sh, 284 (6160)
$[Co(N_4)(H_2O)_2](ClO_4)_2$	H_2O	545 (3450), 358[b]
$[Co(N_4)(H_2O)_2](ClO_4)_3$	H_2O	510[b], 310[b]
$[Co(N_4)Cl_2]ClO_4$	CH_3CN	570[b], 430[b], 395 (1000)
$[Co(N_4)Br_2]ClO_4$	CH_3OH	595[b], 393 (2700), 306 (20000)

[a] Molar absorptivities (cm^{-1}-$\underline{M}^{-1}$) in parentheses.

[b] Molar absorptivity not determined.

[c] sh = shoulder.

The spectrum of $(CH_3)_2Co((1\text{-})N_4)$ (Figure 5) is in agreement with that reported by Witman (69). It consists of two well-resolved bands at 405 and 236 nm and a partially resolved shoulder at 276 nm. The molar absorptivity value determined in acetonitrile (7220 cm^{-1}-$\underline{M}^{-1}$) is quite different from that reported in 2-propanol (8380 cm^{-1}-$\underline{M}^{-1}$).

The spectrum of $[(CH_3)_2Co(N_4)]ClO_4$ (Figure 6) in acetonitrile is similar in appearance to the spectrum of $(CH_3)_2Co((1\text{-})N_4)$. There are two well-resolved bands at 442 and 252 nm and an unresolved shoulder at about 290 nm. The position and intensity of the 442 nm (ε = 8630 cm^{-1}-$\underline{M}^{-1}$) band have not been reported in the literature, so a direct comparison cannot be made; however, it is in agreement with the value obtained for $(CH_3)_2Co((1\text{-})N_4)$. The lower energy position of the absorption maximum (442 vs. 405 nm) is consistent with (N_4) being a weaker in-plane donor than $((1\text{-})N_4)$.[3]

Because the origin of the absorption bands in the spectrum of the dimethyl complexes has not been reported, an assignment of the bands is unwarranted. Comparison to the spectra of the monomethyl complexes however, does allow some conjecture to be made.

The electronic spectra of both monomethyl complexes (Figures 7 and 8) are typical for complexes containing a

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[3]The values of Dq^{xy} (ligand field splitting parameter) support this. Using the method of Wentworth and Piper (96) and assuming C = 3800 cm^{-1} and $Dq^z(Cl^-)$ = 1460 cm^{-1}, $Dq^{xy}((1\text{-})N_4)$ = 3000 cm^{-1} > $Dq^{xy}(N_4)$ = 2780 cm^{-1}.

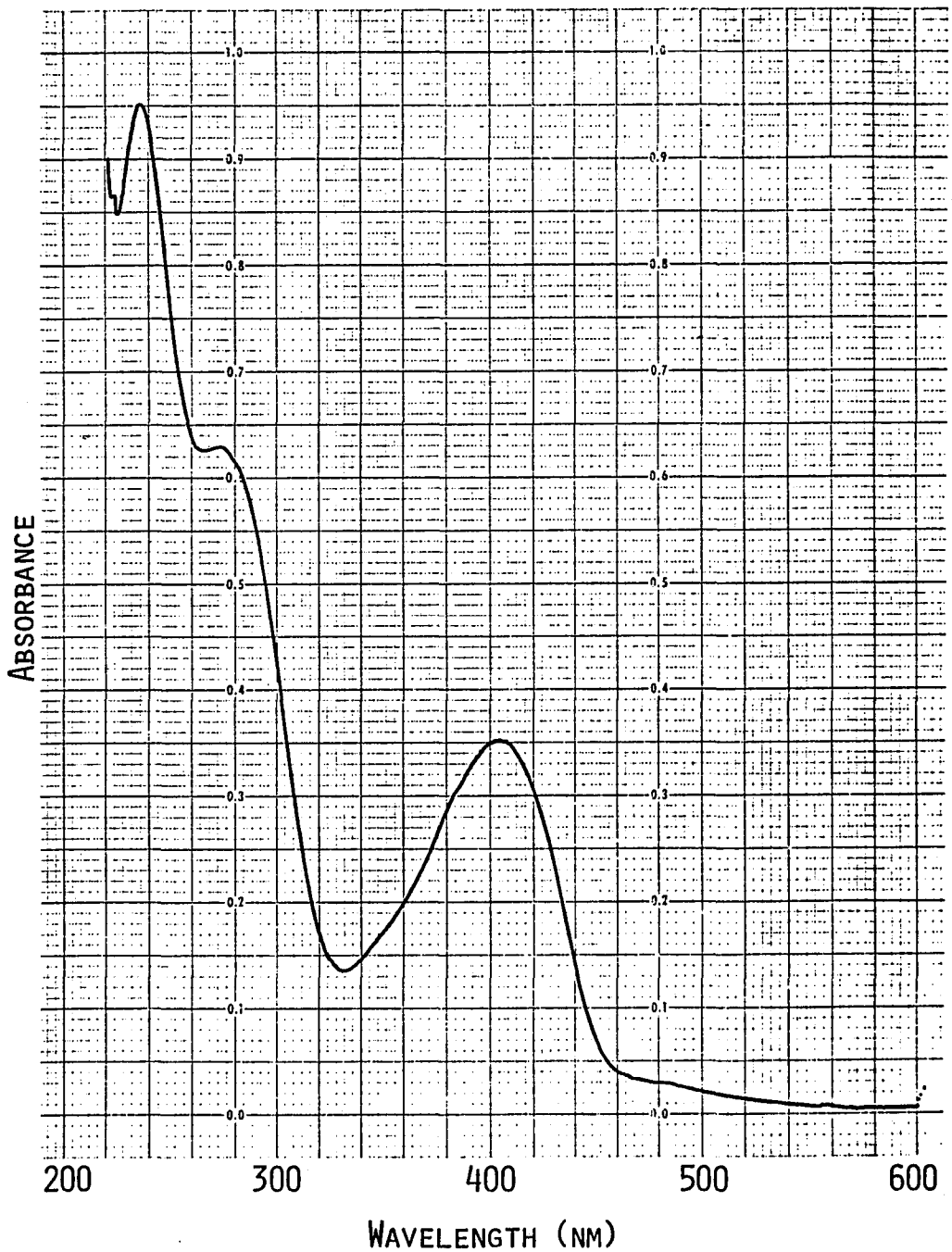


Figure 5. Electronic spectrum of $(CH_3)_2Co((1-)N_4)$ in acetonitrile.

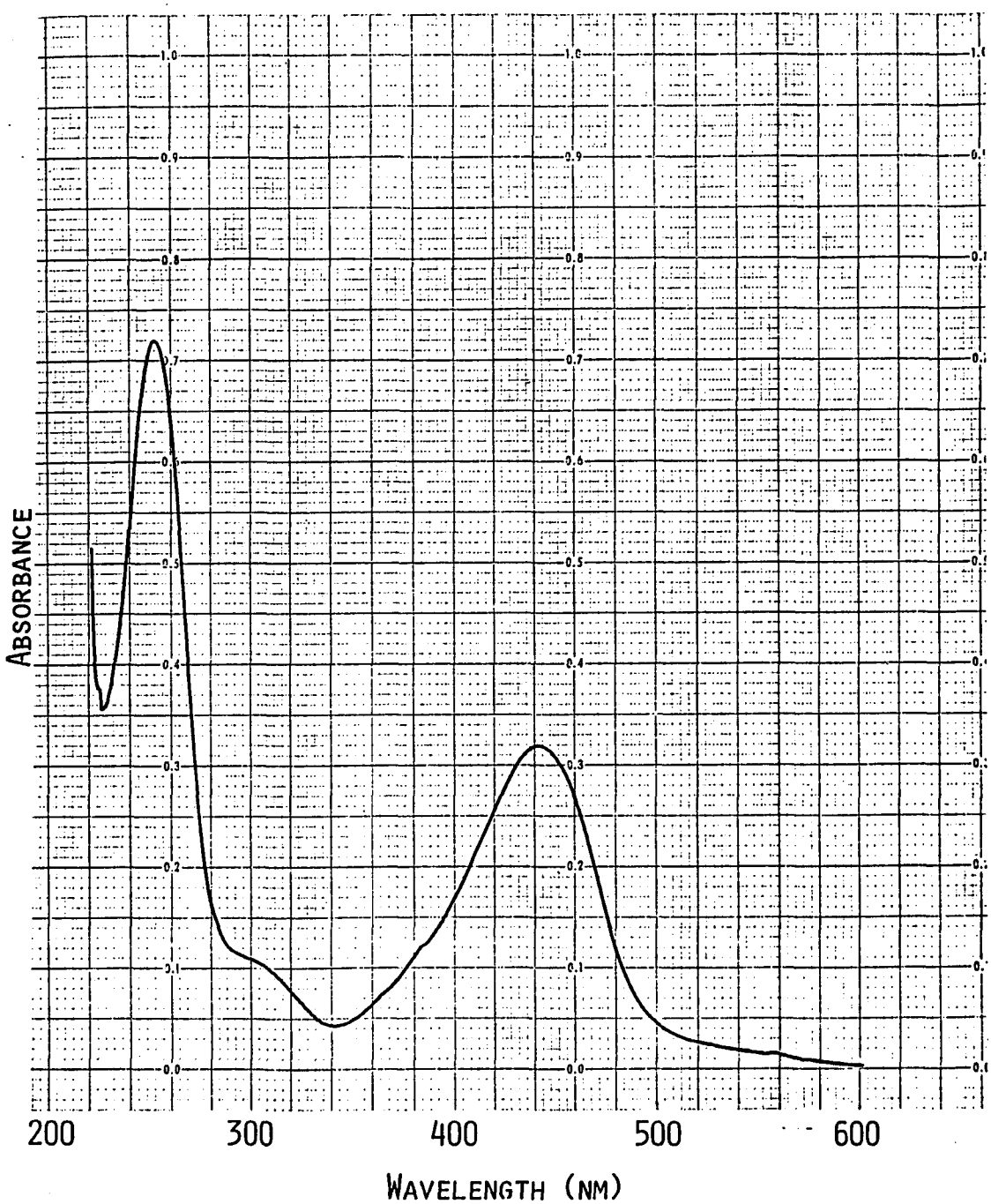


Figure 6. Electronic spectrum of $[(CH_3)_2Co(N_4)]ClO_4$ in acetonitrile.

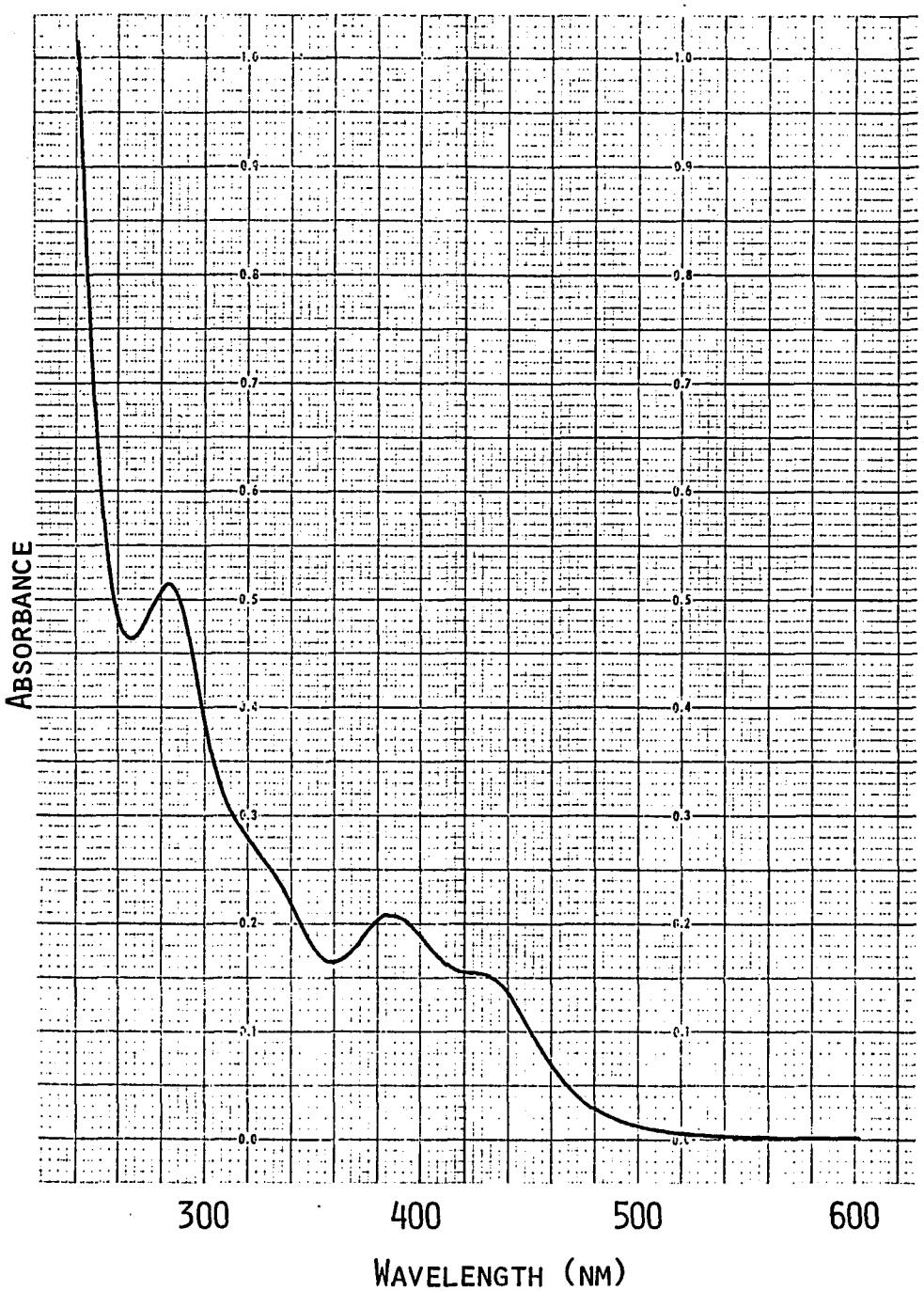


Figure 7. Electronic spectrum of $[CH_3Co((1\text{-})N_4)(CH_3CN)]\text{-}ClO_4$ in acetonitrile.

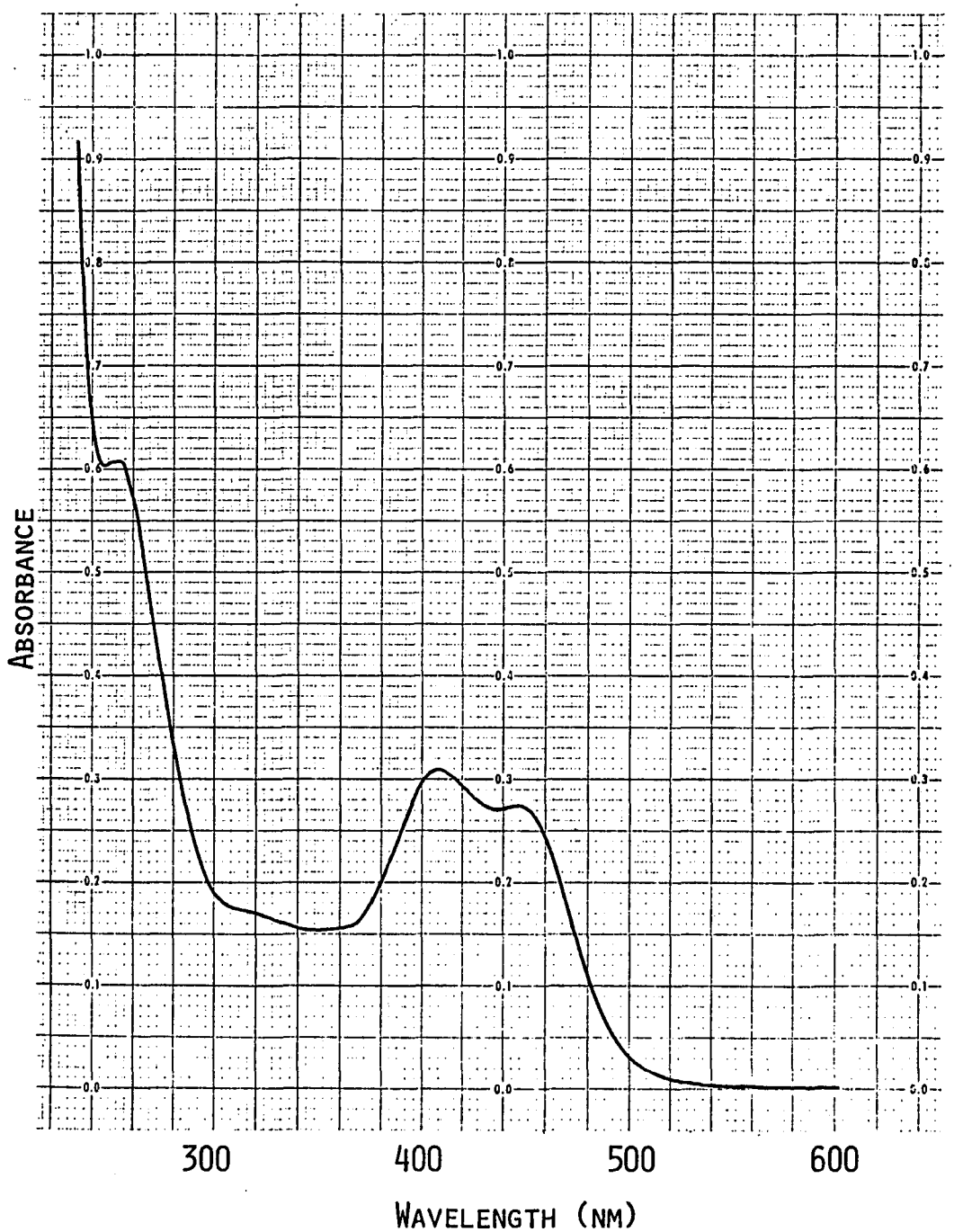


Figure 8. Electronic spectrum of $[CH_3Co(N_4)(CH_3CN)](ClO_4)_2$ in acetonitrile.

coordinated α-diimine macrocycle (42, 97, 98). The spectrum is dominated by an intense charge-transfer (CT) absorption in the UV and two much weaker absorptions in the visible region. The origin of the two low energy bands is debatable. Arguments have been presented for both cobalt-carbon CT (99) and d-d (98) transitions. It is logical to assume that the same arguments could be extended to the spectra of the dimethyl complexes. The CT band in the UV region for both dimethyl complexes is most likely due to the macrocyclic ligand. This is confirmed by comparing the spectra of the dimethyl complexes and monomethyl complexes and noting the similarity in the UV region of each spectrum. It has been suggested that the origin of this CT absorption is the coordinated imines of the macrocycle (100).

Infrared Spectra

The IR spectra of $(CH_3)_2Co((l\text{-})N_4)$ and $[(CH_3)_2Co(N_4)]ClO_4$ were recorded in the 4000-250 cm^{-1} range. The infrared spectra of the dihalide complexes, $[Co(N_4)X_2]ClO_4$ and $Co((l\text{-})N_4)Br_2$, were also recorded to aid in the identification of the ligand bands. The IR data is listed in Table 4.

In accord with the assignments by Witman and Weber (47) of $\nu(Co\text{-}CH_3)$ (488 cm^{-1}) and $\nu(Co\text{-}CD_3)$ (467 cm^{-1}), the absorption at 465 cm^{-1} in the spectrum of $[(CH_3)_2Co(N_4)]ClO_4$ has been assigned as the cobalt-carbon stretching

TABLE 4

INFRARED ABSORPTION FREQUENCIES (cm^{-1})[a]

Complex	ν_s(C-H) and ν_a(C-H)	δ(oxime H-O)	ν(C=N)
$[Co(N_4)Br_2]ClO_4$	2950(w), 2930(m), 2880(w)	---	1580(w)
$[Co(N_4)Cl_2]ClO_4$	2960(w), 2930(sh,m), 2880(w)	---	1590(s)
$[(CH_3)_2Co(N_4)]ClO_4$	2940(m), 2930(m), 2895(m)	---	1510(w)
$Co((1-)N_4)Br_2$	2960(w), 2930(sh,m), 2895(w)	1770(w)	1520(s,br)
$(CH_3)_2Co((1-)N_4)$	2950(m), 2930(m), 2870(m)	1785(w)	1465(s)

[a] s = strong; m = medium; w = weak; sh = sharp; br = broad

TABLE 4 - Continued[a]

Complex	$\delta_{as}(CH_3)$	$\delta_s(CH_3)$	ν_{as}(N-O)	ν_s(N-O)	ν(chelate ring)
$[Co(N_4)Br_2]ClO_4$	1450(m)	1365(m)	---	---	1210(s)
$[Co(N_4)Cl_2]ClO_4$	1425(m)	1365(s)	---	---	1210(s)
$[(CH_3)_2Co(N_4)]ClO_4$	1425(m)	1365(m)	---	---	1210(s)
$Co((1\text{-})N_4)Br_2$	1420(m)	1350(m)	1240(s)	1135(s)	---
$(CH_3)_2Co((1\text{-})N_4)$	1420(m)	1360(m)	1230(m)	1140(s)	---

[a] s = strong; m = medium; w = weak; sh = sharp; br = broad.

TABLE 4 - Continued[a]

Complex	δ(OH)	ν(Co-N)	ν(Co-CH_3)	ν(ClO_4)
$[Co(N_4)Br_2]ClO_4$	---	b	---	1090(s), 920(w), 620(s)
$[Co(N_4)Cl_2]ClO_4$	---	b	---	1090(s), 920(w), 620(s)
$[(CH_3)_2Co(N_4)]ClO_4$	---	b	465(m)	1090(s), 920(w), 620(s)
$Co((l\text{-})N_4)Br_2$	870(s)	525(m), 510(m), 470(s), 430(m)	---	---
$(CH_3)_2Co((l\text{-})N_4)$	870(s)	540(w), 510(w), 440(m)	482(m)	---

[a] s = strong; m = medium; w = weak; sh = sharp; br = broad.

[b] Not observed.

frequency in this complex. Because a deuterated analog was not prepared, confirmation of this assignment by observing the low-frequency shift of $\nu(Co-CD_3)$ in the methyl-d_3 derivative could not be done. The position of this absorption, however, agrees with the reported relationship between $\nu(Co-CH_3)$ and the σ-donor strength of the ligand in the trans position in cobaloximes (46). An increase in the donor strength results in a high-frequency shift of $\nu(Co-CH_3)$. The very large shift observed in these dimethyl complexes, as compared to $\nu(Co-CH_3)$ = 320-350 cm^{-1} in $CH_3Co([14]tetraenato(2-)N_4)L$, is a manifestation of the superior donor strength of a methyl group over ligands such as $P(C_6H_5)_3$ and pyridine.

The high-frequency shift of $\nu(Co-CH_3)$ that is observed in these dimethyl complexes is not expected. One might predict that as the electron density on cobalt increased, as in the series $CH_3Co(chel)X$, X = H_2O, pyridine, CH_3, that the cobalt-carbon bond would weaken, and $\nu(Co-CH_3)$ would decrease. This, however, does not take into account the effect the equatorial ligand might have on the charge density on the metal. Burger et al. (101) demonstrated that $\nu(C=N)$ in oxime ligands shifts to lower frequencies upon complexation. The magnitude of the shift is dependent on the extent of backbonding occurring between the metal d-orbital electrons and the antibonding π-orbitals of the ligand. For the complexes in this study

ν(C=N) is seen at 1580 cm^{-1} ($[Co(N_4)Br_2]ClO_4$), 1520 cm^{-1} ($Co((1\text{-})N_4)Br_2$), 1510 cm^{-1} ($[(CH_3)_2Co(N_4)]ClO_4$), and 1465 cm^{-1} ($(CH_3)_2Co((1\text{-})N_4)$). Comparing these frequencies to ν(C=N) in free oximes and imines (1690-1640 cm^{-1}) demonstrates that significant backbonding is occurring and that much of the electron density that is built up on the cobalt by the presence of the two methyl groups is dissipated out to the ligand. As a result, the cobalt-carbon bond is stronger than anticipated, as is observed spectroscopically.

The presence of two bands at almost identical frequencies (1425 and 1365 cm^{-1}) in the spectra of all five complexes listed in Table 4 is consistent with their assignment as asymmetric and symmetric deformation vibrations due to the equatorial methyls of both ligands. The band present at 1210 cm^{-1} in the spectra of the (N_4) complexes is characteristic for that particular ligand system. The band is considered to be due to vibrations of the five-membered chelate ring of (N_4) (92). This band is seen in the IR spectra of all (N_4) complexes, regardless of the metal ion present. The bands assigned by Witman (69) as arising from Co-N stretch (540-430 cm^{-1}) were not observed in the (N_4) spectrum. It is possible that they are shifted to slightly higher frequencies and are obscured by the very strong bands due to perchlorate ion. Other bands due to C-H, C-C, and C-N vibrations are listed in Table 4 and are self-explanatory.

NMR Spectra

The ^{1}H-NMR spectra of $[(CH_3)_2Co(N_4)]ClO_4$ and $(CH_3)_2Co((1-)N_4)$ were recorded in acetonitrile-d_3 (Figures 9 and 10). The chemical shifts (ppm downfield from TMS) for both dimethyl complexes and the corresponding monomethyl complexes are listed in Table 5.

The signal due to the axial methyl groups appears at 0.07 ppm for $(CH_3)_2Co((1-)N_4)$ and 0.35 ppm for $[(CH_3)_2Co(N_4)]ClO_4$. The shift values agree with those reported for $(CH_3)_2Co((1-)N_4)$ (40) and for $[(CH_3)_2Co(N_4)]$-$B(C_6H_5)_4$ (36). The high-field position of these signals confirms that the axial methyls are bound directly to cobalt. Shift values of less than 1 ppm are typical for methylcobalt complexes (36). The variation in the methyl resonance position between the complexes is a reflection of the electron density differences on cobalt due to the different donor properties of the equatorial ligands. The observed order of axial methyl shift values, (N_4) > $((1-)N_4)$, is in agreement with the order of increasing electron density on cobalt, $((1-)N_4)$ > (N_4).

The other resonances present in the spectra of the complexes correspond to the protons of the macrocycles. Their assignments were made on the basis of the integration values and the reported spectra of $[CH_3Co((1-)N_4)$-$(H_2O)]ClO_4$ (41) and $[Co(N_4)Cl_2]PF_6$ (83).

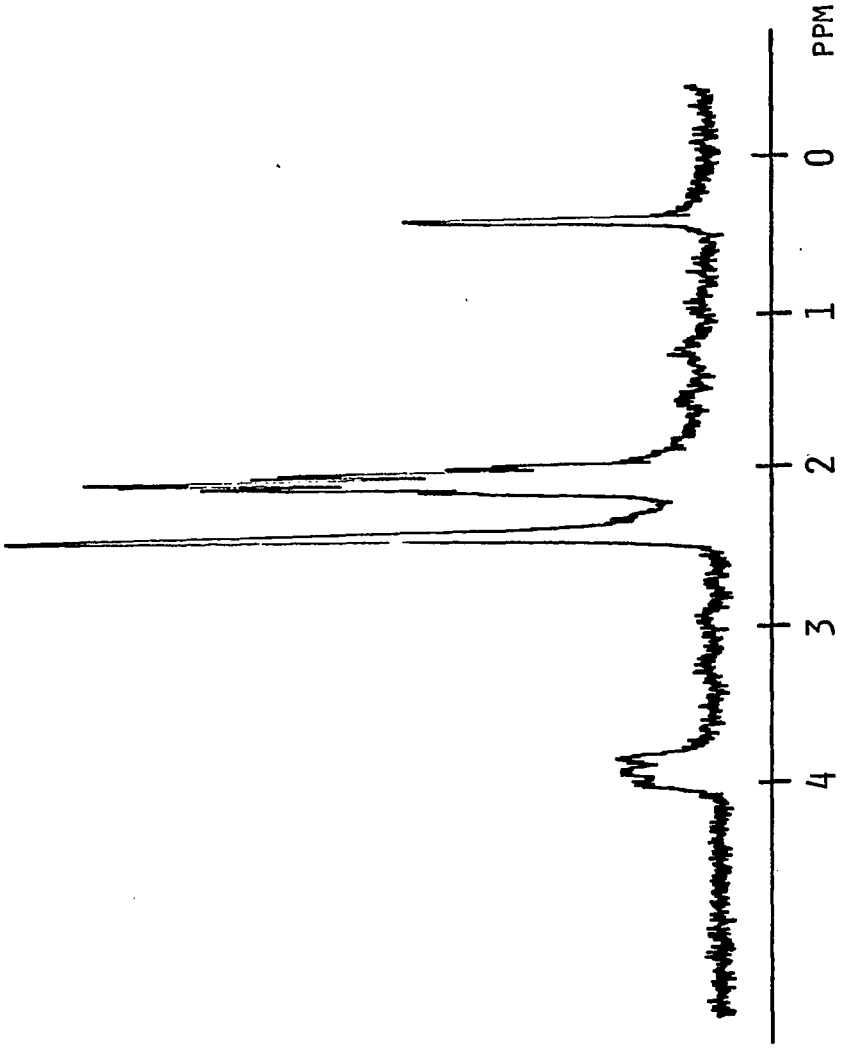


Figure 9. ^{1}H-NMR spectrum of $[(CH_3)_2Co(N_4)]ClO_4$ in acetonitrile-d_3.

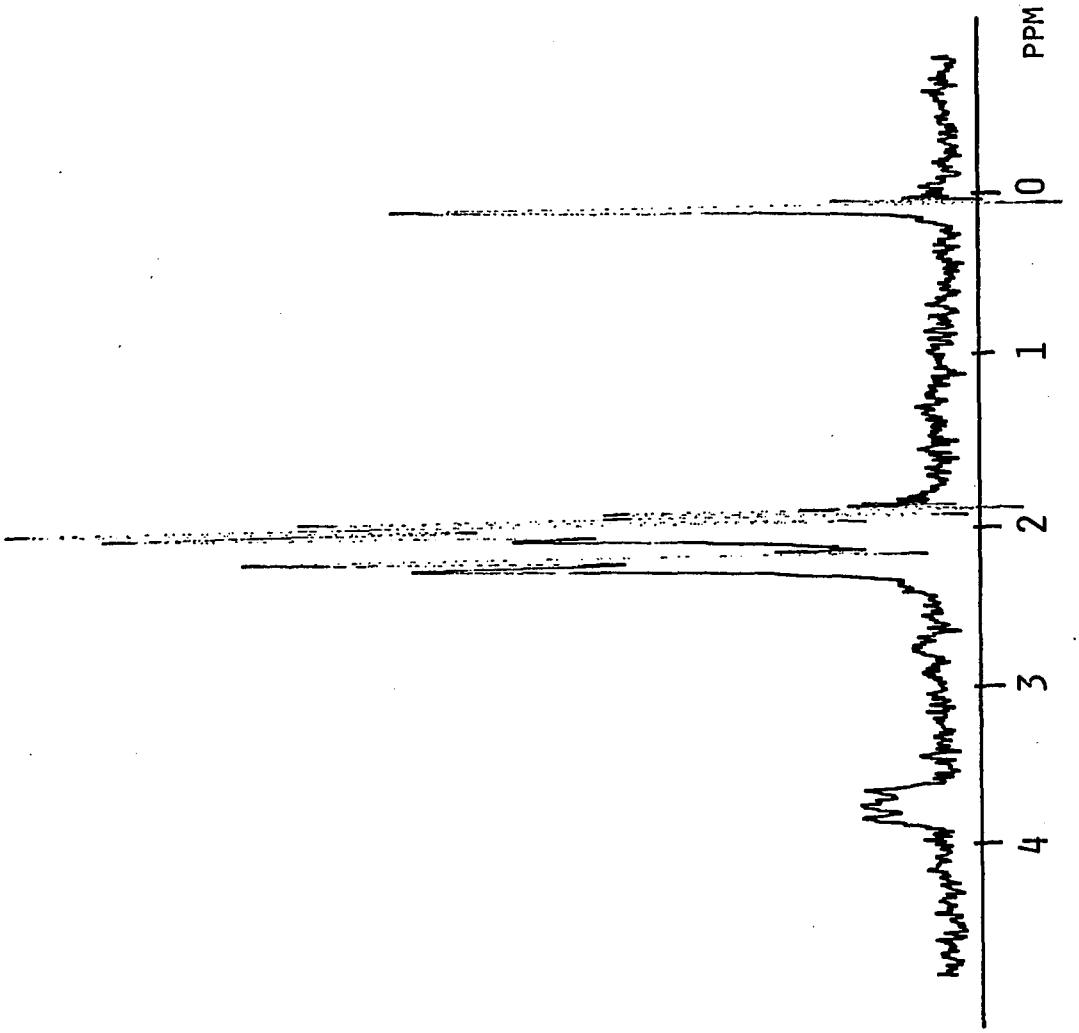


Figure 10. ^{1}H-NMR spectrum of $(CH_3)_2Co((1-)N_4)$ in acetonitrile-d_3.

TABLE 5

^{1}H-NMR DATA[a]

Complex	Chemical Shift (ppm)[b]	Multiplicity[c]	Assignment
$(CH_3)_2Co((1\text{-})N_4)$	0.07	singlet (6)	Co-$\underline{CH}_3$
	2.35	singlet	N=C-$\underline{CH}_3$
	2.36	singlet (14)	N=C-$\underline{CH}_3$
	2.4 - 2.1	multiplet	C-$\underline{CH}_2$-C
	3.8	triplet (4)	N-$\underline{CH}_2$-C
$[CH_3Co((1\text{-})N_4)(CH_3CN)]ClO_4$	0.85	singlet (3)	Co-$\underline{CH}_3$
	2.25	singlet (6)	CH_2-N=C-$\underline{CH}_3$
	2.35	singlet (6)	O-N=C-$\underline{CH}_3$
	3.75	multiplet (4)	N-$\underline{CH}_2$-C

[a] All spectra run in acetonitrile-d_3.

[b] Chemical shifts relative to TMS.

[c] Integration indicated in parentheses.

TABLE 5 - Continued

Complex	Chemical Shift (ppm)[b]	Multiplicity[c]	Assignment
$[(CH_3)_2Co(N_4)]ClO_4$	0.35	singlet (6)	$Co-CH_3$
	2.40	singlet (16)	$N=C-CH_3$
	2.15 - 2.45	multiplet	$C-CH_2-C$ (β)
	3.85	triplet (8)	$N-CH_2-C$ (α)
$[CH_3Co(N_4)(CH_3CN)](ClO_4)_2$[d]	1.30	singlet (3)	$Co-CH_3$
	2.45	singlet (12)	$N=C-CH_3$
	3.85	triplet (8)	$N-CH_2-C$ (α)

[a] All spectra run in acetonitrile-d_3.

[b] Chemical shifts relative to TMS.

[c] Integration indicated in parentheses.

[d] β-protons obscured by solvent peak.

Characterization of the Methyllead Compounds

The methyllead compounds, $(CH_3)_3PbCl$ and $(CH_3)_2Pb(NO_3)_2$, were synthesized from $(CH_3)_4Pb$ by literature procedures as outlined in the Experimental Section. The elemental analysis of $(CH_3)_3PbCl$ agreed with the theoretical values but that of $(CH_3)_2Pb(NO_3)_2$ consistently showed the compound to be low in nitrogen. The use of various catalysts (e.g., tungstic oxide) did not alter the results (i.e., Calcd: 7.76%. Found: 6.02%). This was rather intriguing because the observed carbon, hydrogen, and lead percentages were always in excellent agreement. Determination of the nitrate content of the compound (Calcd for NO_3^-: 34.35%. Found: 34.65%) also supports the contention that the compound is pure $(CH_3)_2Pb(NO_3)_2$. The reason for the apparent loss of nitrogen upon combustion in the furnace is not obvious. The possibility that some nonvolatile lead-nitrogen compound is being formed cannot be ruled out.

The organolead compounds which were prepared were characterized by IR and ^{1}H-NMR spectroscopy. Each of these characterizations will be summarized briefly.

The chemical shift values from the ^{1}H-NMR spectrum obtained for each methyllead compound are listed in Table 6. The chemical shift and $J(^{207}Pb\text{-}H)$ for cationic methyllead(IV) compounds are highly solvent-dependent (89, 102, 103, 104). The chemical shift of the methyl protons moves to higher magnetic field and $J(^{207}Pb\text{-}H)$ increases as the

TABLE 6

METHYLLEAD NMR SHIFT DATA

Compound	Solvent	$\delta(CH_3)^a$	$J(^{207}Pb\text{-}H)^b$
$(CH_3)_4Pb$	toluene/CD_3CN	0.75	62
$(CH_3)_3PbCl$	CD_3CN	1.50	79
$(CH_3)_2Pb(NO_3)_2$	CD_3CN	2.65	140
$Pb_2(CH_3)_6$[c]	toluene	1.00	42, 23

[a] ppm positive to low field of TMS.

[b] Coupling constants in Hz.

[c] Data from ref 104.

donor strength of the solvent molecule increases. For example, for $(CH_3)_2Pb(NO_3)_2$, $\delta(CH_3)$ = 2.33 ppm in $(CH_3)_2SO$, 2.42 ppm in H_2O, and 3.20 ppm in 70% $HClO_4$. The values of $J(^{207}Pb\text{-}H)$ vary from 148 Hz to 101 Hz over the same range of solvents. In acetonitrile-d_3, $(CH_3)_2Pb(NO_3)_2$ exhibits a resonance at 2.65 ppm that is split, with a J value of 140 Hz; $(CH_3)_3PbCl$ shows a resonance at 1.50 ppm that is split, with a J value of 79 Hz.

The IR spectra of the methyllead compounds were obtained in the 4000-250 cm^{-1} range. The results shown in Table 7 agree with the literature (105, 106, 107).

Reactions of $(CH_3)_2Co(chel)$ with Metallic Electrophiles

The dealkylation of organocobalt complexes by metallic electrophiles has been a subject of considerable interest for many years. This interest is presumably due to the suspected involvement of methylcobalamin in the biotransformation of inorganic metal ions such as Hg^{2+} and Pb^{2+} into highly toxic organometallic species (108). Despite the ready cleavage of the cobalt-carbon bond in methylcobalamin and other synthetic monoorganocobalt complexes by Hg^{2+}, Tl^{3+}, and Cr^{2+} (50, 51, 58), these complexes are essentially unreactive toward dealkylation by other electrophiles such as Pb^{2+}, Cr^{3+}, Cd^{2+}, Zn^{2+}, or CH_3Hg^+ (16, 58).

TABLE 7

INFRARED FREQUENCIES FOR METHYLLEAD COMPOUNDS (cm^{-1})[a]

Compound	$\nu_{as}(CH_3)$	$\nu_s(CH_3)$	$\delta_{as}(CH_3)$	$\delta_s(CH_3)$	$\rho_r(CH_3)$	$\nu_a(CH_3)Pb$
$(CH_3)_2Pb(NO_3)_2$	3060(m,br)	2940, 2960(sh)	b	1190, 1165(w)	740, 730(sh)	495(s)
$(CH_3)_3PbCl$	3010(m,br)	2920(m,br)	1390(m,br)	1150, 1140(sh)	775, 785(s,br)	490(vsh)

[a] s = strong; m = medium; w = weak; sh = sharp; br = broad; vsh = very sharp.

[b] Obscured by NO_3^- bands.

Addition of a second alkyl group in a position trans to the first alkyl group tends to activate one of the groups toward electrophilic attack. This activation results from the superior trans-labilizing character of an alkyl group relative to other Lewis bases such as pyridine or triphenylphosphine (43, 44). Reports (68, 71, 72) of the demethylation of $(CH_3)_2Co(chel)$ (chel = (N_4), $((1\text{-})N_4)$, $(Me_2pyo[14]trieneN_4)$) by electrophiles such as RHg^+, Cd^{2+}, Zn^{2+}, Pb^{2+}, and $[Co(chel^*)(H_2O)_2]^+$ (chel* = salen, saloph) demonstrate the importance of this effect.

This study involves demethylation of $(CH_3)_2Co(chel)$ by metallic electrophiles in an aprotic solvent (CH_3CN), a comparison of the reactivity differences between $(CH_3)_2Co((1\text{-})N_4)$ and $[(CH_3)_2Co(N_4)]ClO_4$, and the fate of the organometallic species generated in these reactions.

The discussion of this work will be divided into four sections: reaction of $(CH_3)_2Co(chel)$ with Zn^{2+} and Cd^{2+}, reaction of $(CH_3)_2Co((1\text{-})N_4)$ with Pb^{2+}, reaction of $[(CH_3)_2Co(N_4)]ClO_4$ with Pb^{2+}, and reaction of $(CH_3)_2Co((1\text{-})N_4)$ with Cr^{3+} and Cu^{2+}.

Reaction of $(CH_3)_2Co(chel)$ with Zn^{2+} and Cd^{2+}

The demethylation of $(CH_3)_2Co((1\text{-})N_4)$ by Zn^{2+} or Cd^{2+} in 2-propanol has been demonstrated to occur with either a 1:1 (eq 64) or 1:2 (eq 64 and 65) stoichiometry[4] (69).

[4]Reaction stoichiometry is defined as moles of electrophile:moles of dimethyl complex.

$$(CH_3)_2Co((1\text{-})N_4) + M^{2+} \longrightarrow CH_3Co((1\text{-})N_4)^+ + CH_3M^+ \quad (64)$$

$$(CH_3)_2Co((1\text{-})N_4) + CH_3M^+ \longrightarrow CH_3Co((1\text{-})N_4)^+ + (CH_3)_2M \quad (65)$$

When $(CH_3)_2Co(chel)$ is demethylated by Zn^{2+} or Cd^{2+} in acetonitrile, a similar reactivity pattern is found, because spectral titrations confirm the presence of the 1:1 and 2:1 reactions. By means of a rapid titration technique developed in this laboratory (69), attempts were made to titrate the fast first reaction of the overall biphasic reaction. Titration of $(CH_3)_2Co(chel)$ with Zn^{2+} or Cd^{2+} did not yield the 1.0 endpoint predicted by eq 66, but rather values between 1.0 and 0.5. The low endpoints reflect the partial reaction of CH_3M^+ formed in eq 66 with a second mole of the dimethyl complex (eq 67). Hence the

$$(CH_3)_2Co(chel) + M^{2+} \longrightarrow CH_3Co(chel)^+ + CH_3M^+ \quad (66)$$

$$(CH_3)_2Co(chel) + CH_3M^+ \longrightarrow CH_3Co(chel)^+ + (CH_3)_2M \quad (67)$$

relative reaction rates of eq 66 and 67 allow the steps to be distinguished in 2-propanol (69), but not in acetonitrile. The overall biphasic nature of the reaction was confirmed by slow spectral titration. Plots of absorbance vs. mole ratio = M^{2+}/complex (Figures 11 and 12) yield

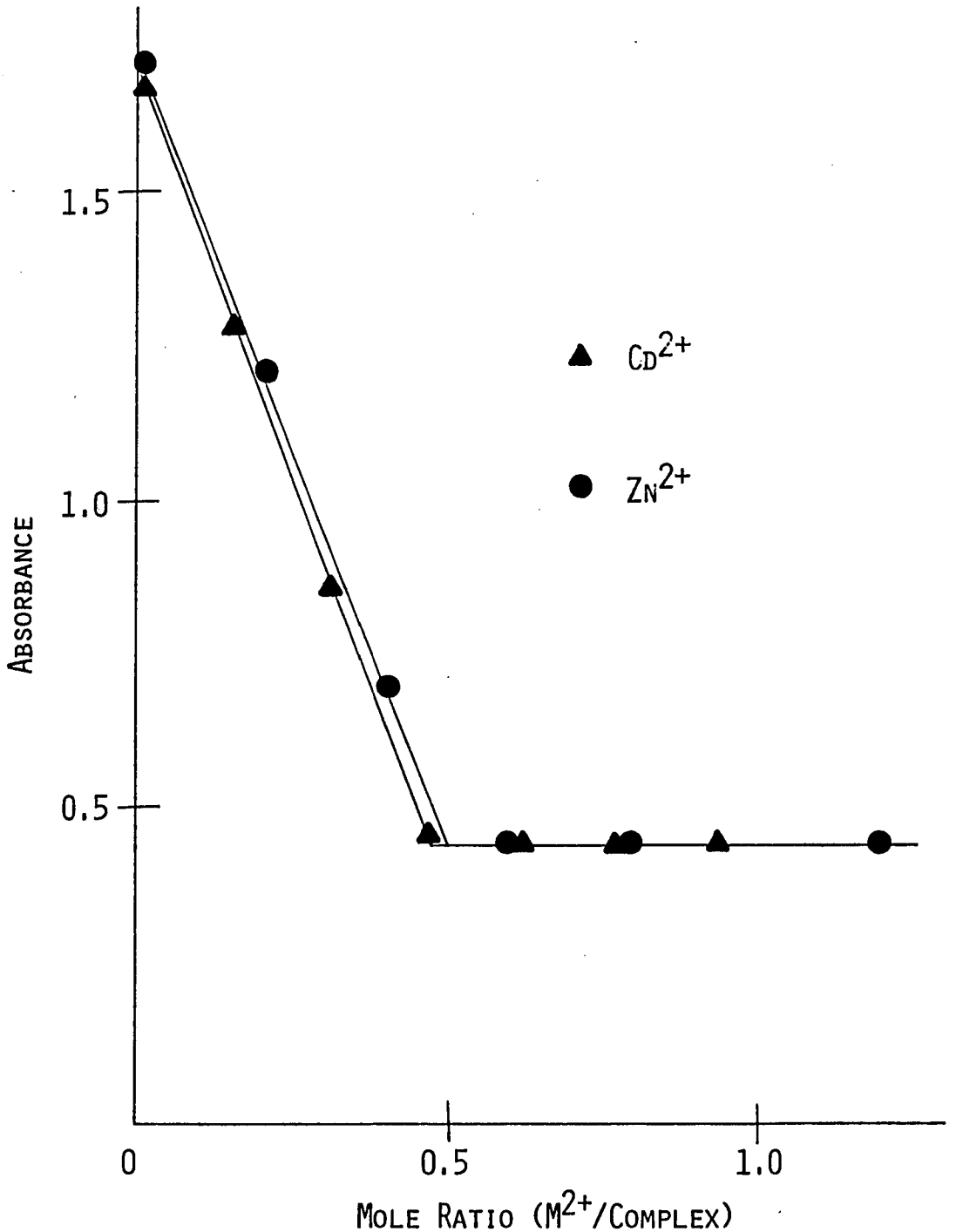


Figure 11. Representative spectral titration of $(CH_3)_2Co((l\text{-})N_4)$ with Zn^{2+} (●) and Cd^{2+} (▲).

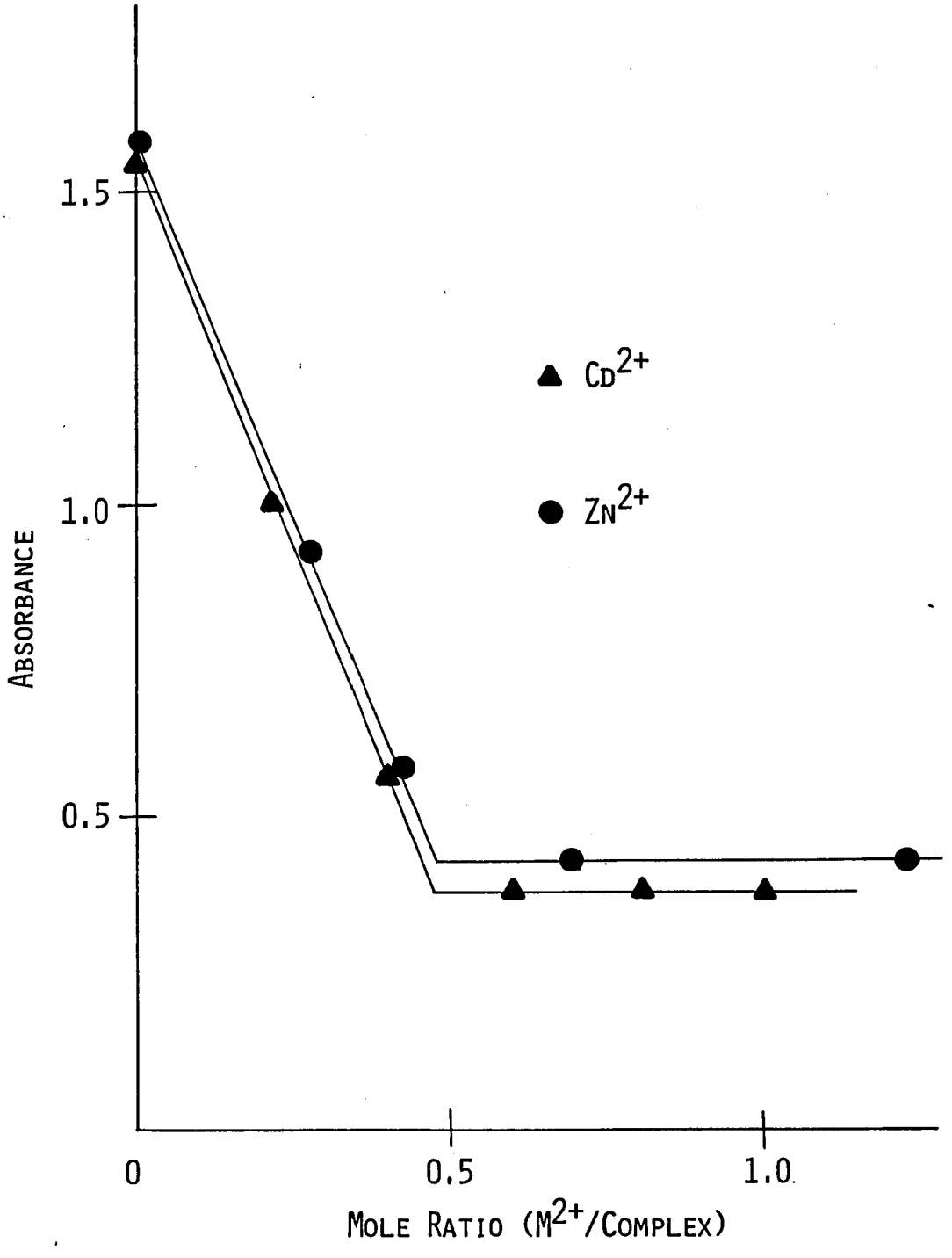


Figure 12. Representative spectral titration of $[(CH_3)_2Co(N_4)]ClO_4$ with Zn^{2+} (●) and Cd^{2+} (▲).

endpoints of 0.5, which are indicative of the 1:2 reaction, in which 1 mole of the metal ion reacts with 2 moles of the dimethyl complex (eq 66 and 67).

Evidence to support the proposed reaction scheme and the formation of CH_3M^+ and $(CH_3)_2M$ intermediates was provided by a series of NMR titrations in acetonitrile-d_3. The addition of an equimolar or excess quantity of Zn^{2+} to an anaerobic solution of $(CH_3)_2Co(chel)$ in an NMR tube resulted in the instantaneous disappearance of the resonance due to the two methyl groups bound to cobalt and the appearance of two new resonances (Figure 13). The resonance on the low-field side of the TMS is due to the one remaining group bound to cobalt and the resonance on the high-field side of TMS is attributed to the presence of solvated CH_3Zn^+ (-0.85 ppm). The assignment of this resonance to the monomethyl species is in agreement with the literature (109), although it appears at a slightly higher field than has been reported.

When the NMR spectra of solutions made from Zn^{2+} and excess $(CH_3)_2Co(chel)$ (mole ratio = 0.5) were examined, no resonance attributable to $(CH_3)_2Zn$ was observed (Figure 14). A resonance at -0.85 ppm due to CH_3Zn^+ was observed immediately after the addition of the Zn^{2+}, but it had disappeared within two minutes. The only other change noted was the immediate appearance of a methane peak at +0.20 ppm after initiation of the reaction.

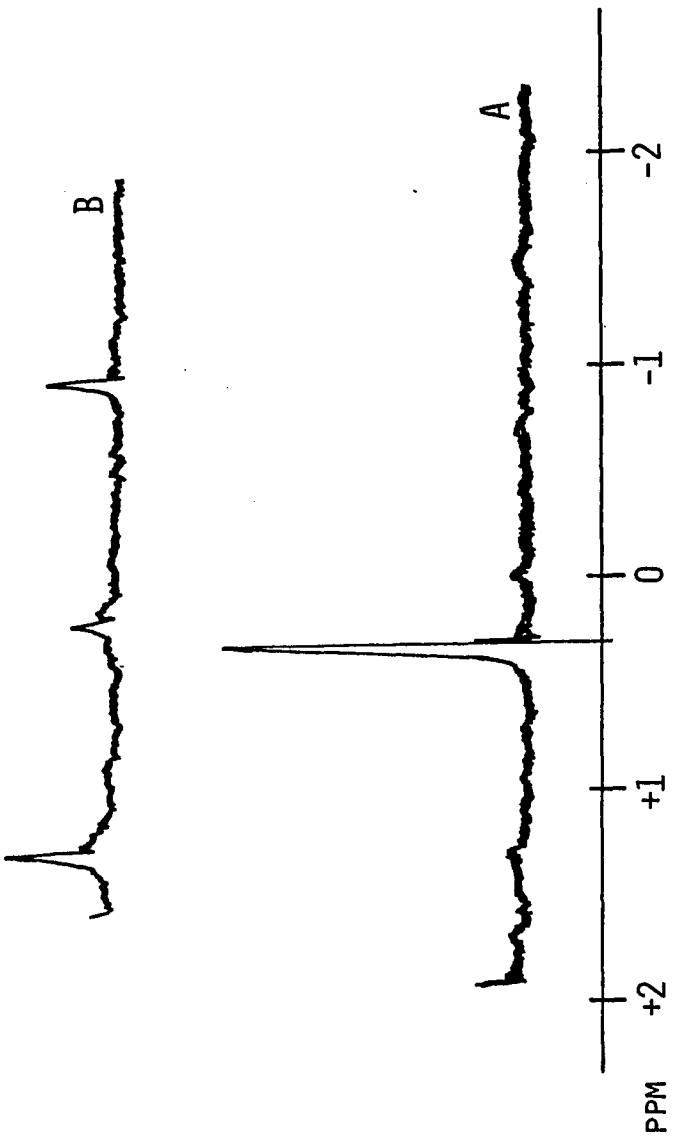


Figure 13. The ^{1}H-NMR spectrum between +2.0 and -2.0 ppm of (A) $[(CH_3)_2Co(N_4)]^+$ and (B) $[(CH_3)_2Co(N_4)]^+$ after the addition of excess Zn^{2+}.

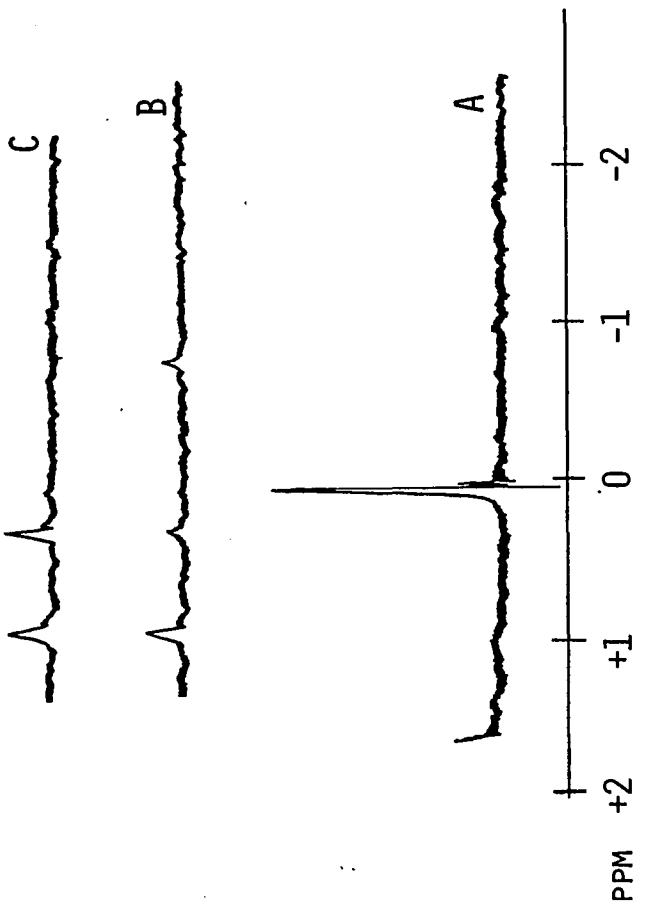


Figure 14. The ^{1}H-NMR spectrum between +2.0 and -2.0 of (A) $[(CH_3)_2Co(N_4)]^+$, (B) $[(CH_3)_2Co(N_4)]^+$ immediately after the addition of Zn^{2+} (mole ratio = 0.5), and (C) two minutes later.

$(CH_3)_2Zn$ is not observed in the NMR spectrum of solutions made from Zn^{2+} and excess $(CH_3)_2Co(chel)$ because of its reactivity under the conditions of this study. The $(CH_3)_2Zn$ instability occurs because acetonitrile acts as a Lewis base toward it and renders it more susceptible to hydrolysis by the water added as hydrated Zn^{2+} (110, 111). This conclusion is reinforced by the instantaneous formation of methane observed in both NMR and GLC (Figure 15) experiments.

The transient appearance of CH_3Zn^+ in the NMR spectra of these reaction mixtures implies that $(CH_3)_2Zn$ is losing both methyls very rapidly. This is intriguing because studies of CH_3Zn^+ generated in solutions of $(CH_3)_2Co(chel)$ and excess Zn^{2+} do not show it to be especially unstable. The rate of methane evolution from a solution of Zn^{2+} and $(CH_3)_2Co(chel)$ (mole ratio $\geq$ 1.0) was determined by GLC. Linear plots of $\ln(C_\infty - C)$ vs. time (Figure 16) indicate that the methane is the product of a first-order process. From this data, the half-life for the decomposition was determined to be 43 min (k_{obs} = 1.61 x 10^{-2} min^{-1}) in the presence of $CH_3Co((1\text{-})N_4)$ and 27 min (k_{obs} = 2.54 x 10^{-2} min^{-1}) in the presence of $CH_3Co(N_4)^{2+}$. This is consistent with a reaction in which CH_3Zn^+ is decomposed by water present in the system (eq 68). Because the water is in excess over CH_3Zn^+, the reaction follows

$$CH_3Zn^+ + H_2O \longrightarrow CH_4 + Zn^{2+} + OH^- \qquad (68)$$

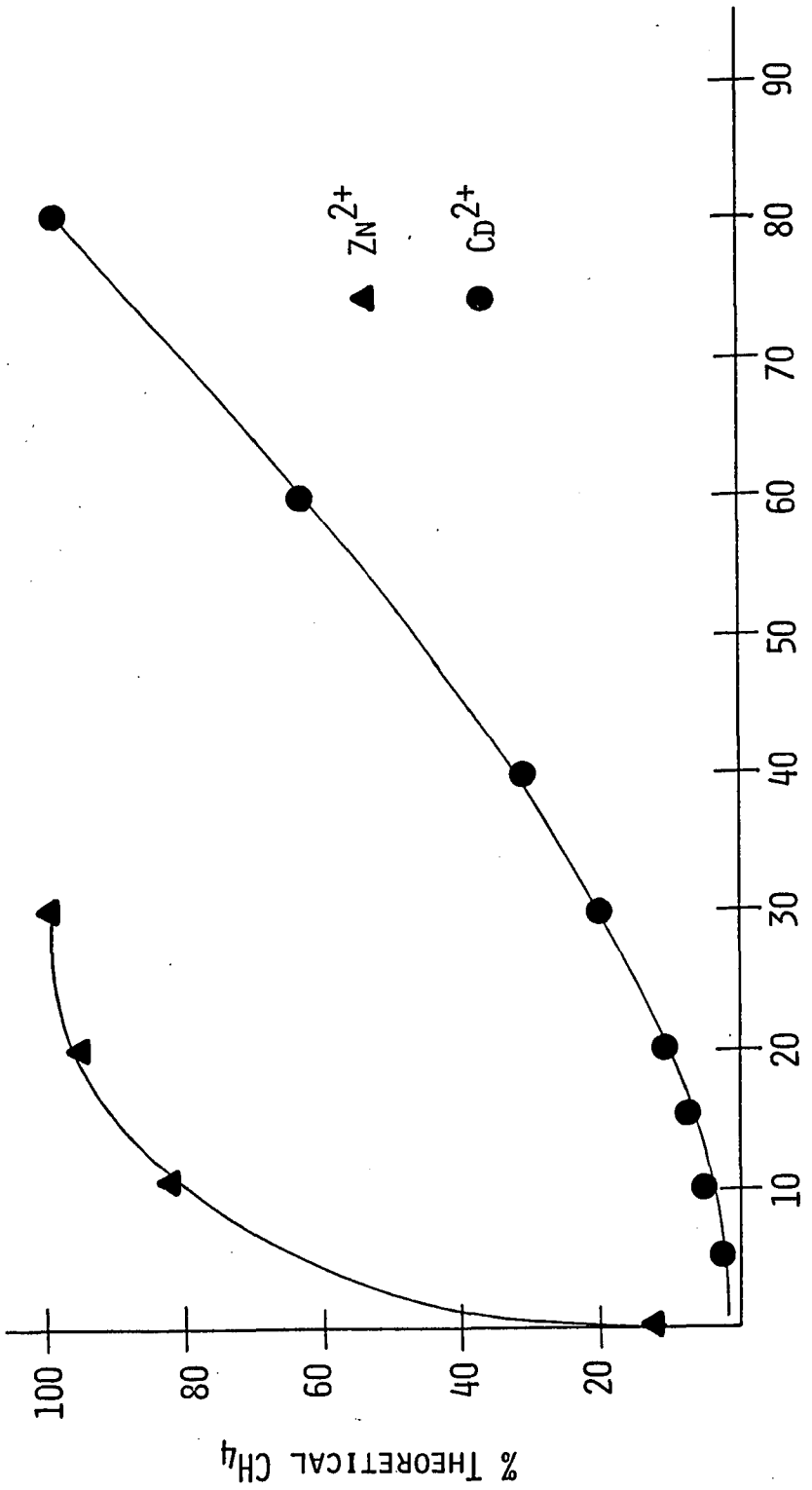


Figure 15. Evolution of methane from the reaction of $(CH_3)_2Co((1\text{-})N_4)$ with Zn^{2+} (▲) and Cd^{2+} (●) (mole ratio = 0.5).

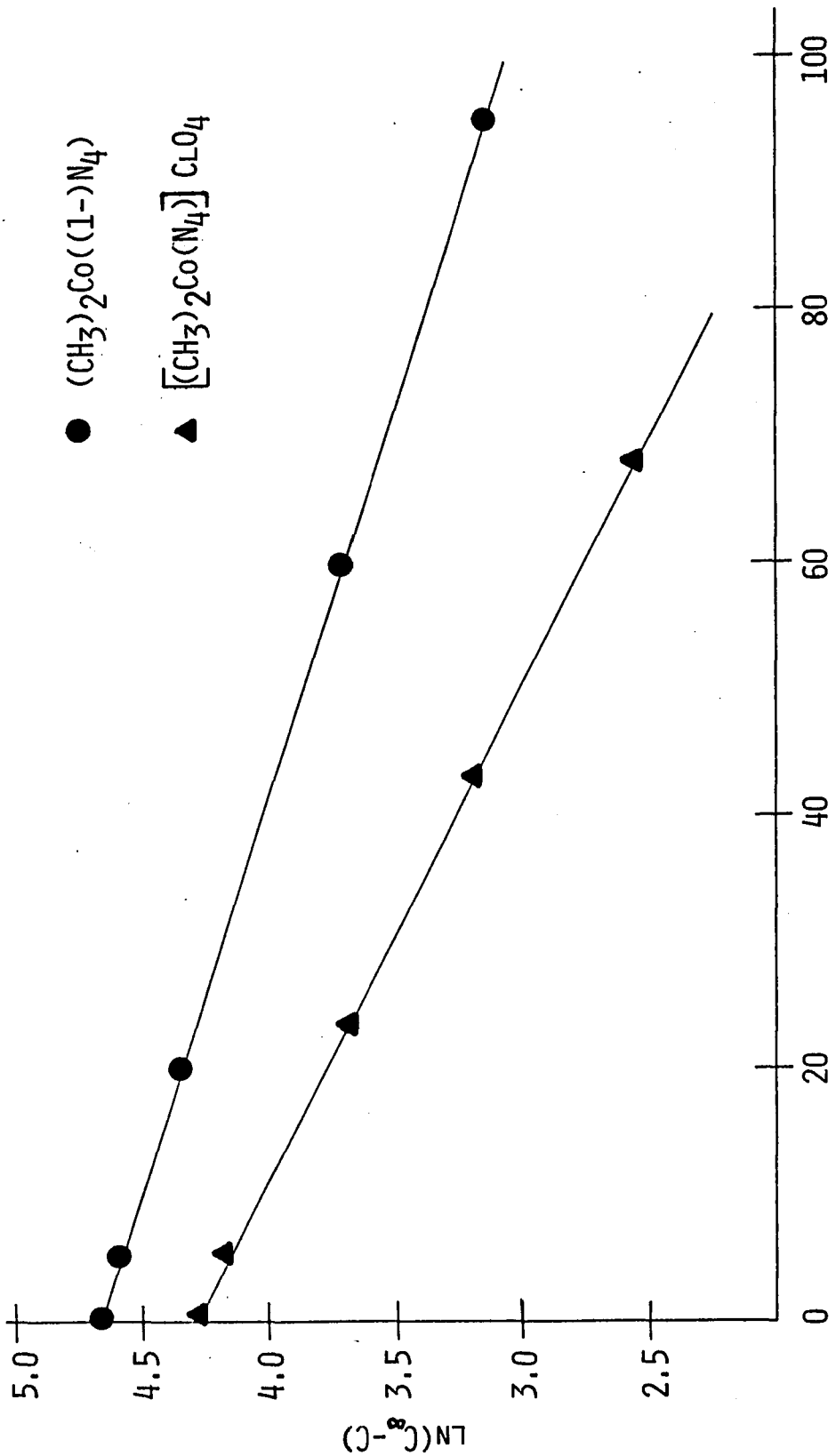


Figure 16. Rate of methane evolution for the reaction of $(CH_3)_2Co((1-)N_4)$ with Zn^{2+} (●) and $[(CH_3)_2Co(N_4)]ClO_4$ with Zn^{2+} (▲) (mole ratio = 4.0).

the observed pseudo first-order kinetics. Additional support for the stability of CH_3Zn^+ under the conditions of this study was gained by observing the decomposition of CH_3Zn^+ in the NMR experiments. The methane resonance appeared slowly (Figure 17).

Dialkylzincs are readily decomposed by substances that contain acidic hydrogen (112). The decomposition appears to proceed in a stepwise manner (eq 69 and 70) because the intermediate monoalkylzincs, such as CH_3ZnOCH_3

$$R_2Zn + H_2O \longrightarrow RZn^+ + RH + OH^- \qquad (69)$$

$$RZn^+ + H_2O \longrightarrow Zn^{2+} + RH + OH^- \qquad (70)$$

and C_2H_5ZnOH, can be isolated from these reactions (113). It is logical to assume that if the decomposition of $(CH_3)_2Zn$ generated in this study is proceeding by a similar pathway, the intermediate CH_3Zn^+ should show the same stability observed above. The very different reactivity seen for the CH_3Zn^+ in this instance suggests that another decomposition mechanism is in effect.

Studies of Schlenk-type equilibria (eq 71) involving diorganocadmium and cadmium halides have been carried out by means of a variety of techniques (109, 114, 115). All

$$R_2M + M^{2+} \rightleftharpoons 2RM^+ \qquad (71)$$

investigations demonstrated that RCd^+ species are formed and that an equilibrium is established. Evidence obtained

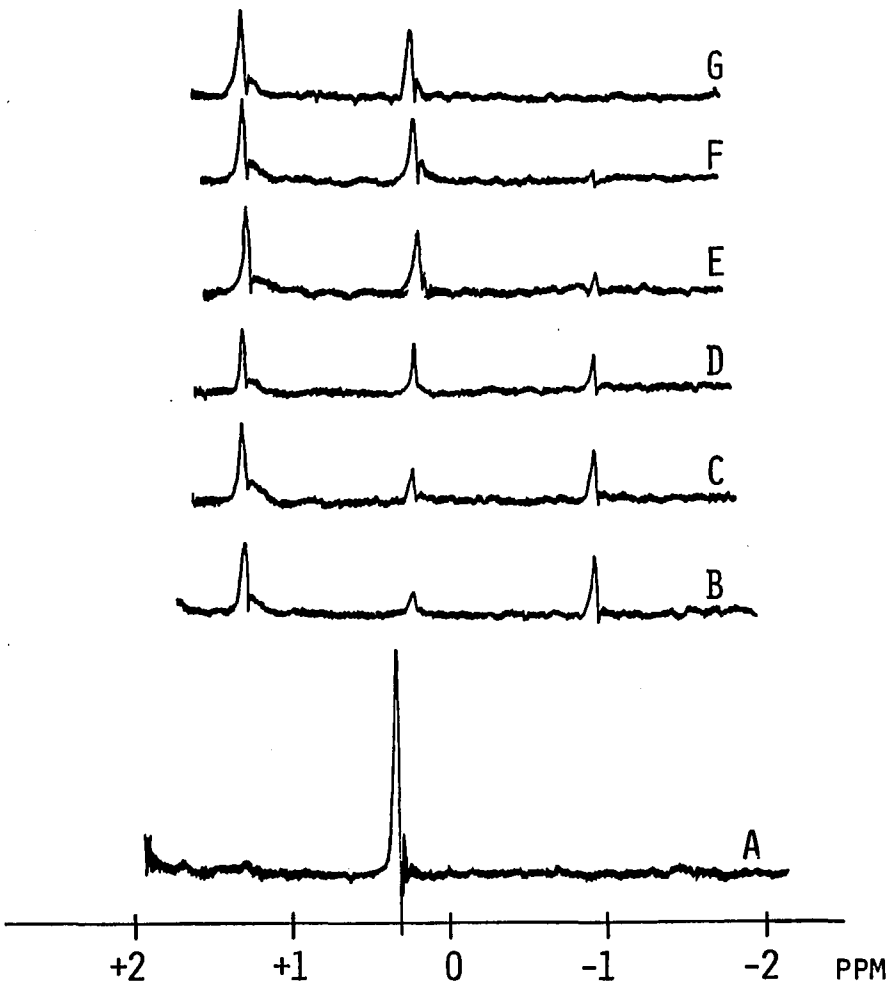


Figure 17. The ^{1}H-NMR spectrum between +2.0 and -2.0 of (A) $[(CH_3)_2Co(N_4)]^+$, (B) immediately after the addition of excess Zn^{2+}; after (C) 6 min, (D) 10 min, (E) 18 min, (F) 25 min, (G) 35 min.

from NMR and GLC experiments supports the existence of a similar equilibrium under the conditions of this study. As a result, attempts to confirm the presence of CH_3Cd^+ in solutions made from $(CH_3)_2Co(chel)$ and an equimolar or excess of Cd^{2+} were complicated by the presence of $(CH_3)_2Cd$.

The addition of an equimolar or excess of Cd^{2+} to an anaerobic solution of $(CH_3)_2Co(chel)$ in an NMR tube resulted in the instantaneous disappearance of the signal due to the $(CH_3)_2Co(chel)$ and the appearance of both the signal due to $CH_3Co(chel)^+$ and a broad resonance on the high-field side of TMS (Figure 18). The high-field resonance is centered at -0.50 ppm and is assigned to CH_3Cd^+ and $(CH_3)_2Cd$ in equilibrium. Roberts and coworkers (114) have reported a similar NMR spectrum for mixtures of $(CH_3)_2Cd$ and $CdBr_2$ in THF. The absence of discrete resonances for each of the organometallic species present is typical of the NMR spectra of methylmetal compounds that are undergoing rapid intermolecular exchange of methyl groups (114, 116-118).

When the NMR spectra of solutions prepared from Cd^{2+} and excess $(CH_3)_2Co(chel)$ (mole ratio = 0.5) were examined (Figure 19), the high-field resonance was observed to be sharper and shifted upfield to -0.60 ppm. This resonance is due to $(CH_3)_2Cd$, and its observed chemical shift agrees with reported values (109). Because the only organocadmium

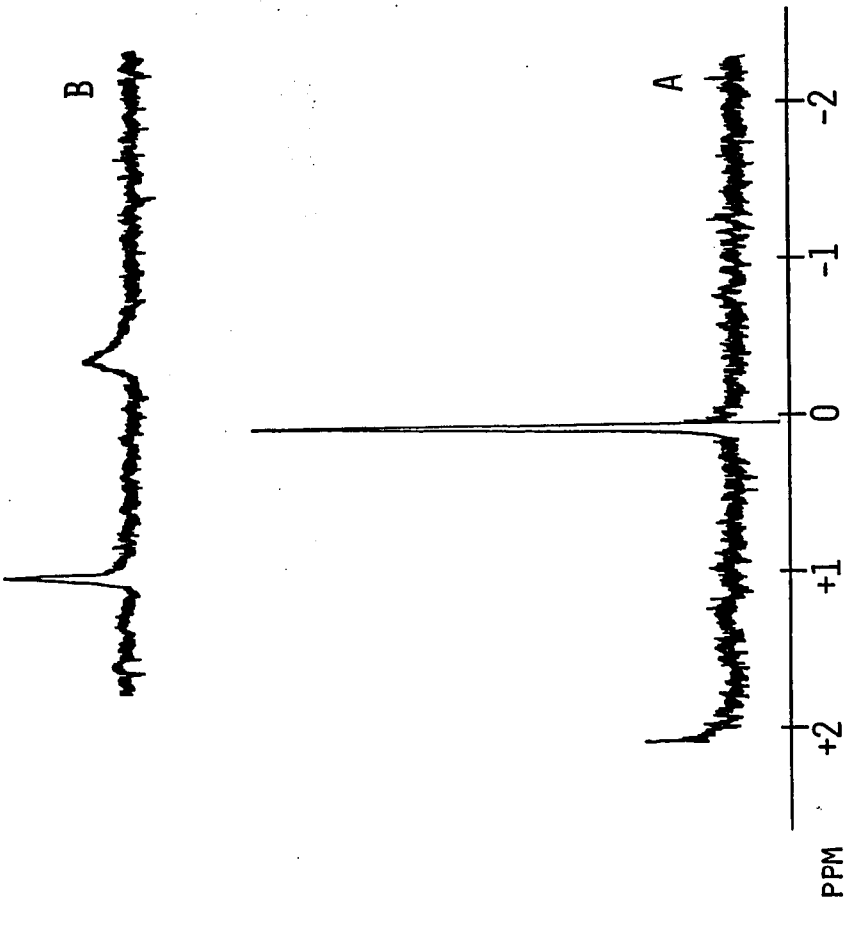


Figure 18. The ^{1}H-NMR spectrum between +2.0 and -2.0 ppm of (A) $[(CH_3)_2Co((1-)N_4)]$ and (B) $[(CH_3)_2Co((1-)N_4)]$ after the addition of excess Cd^{2+}.

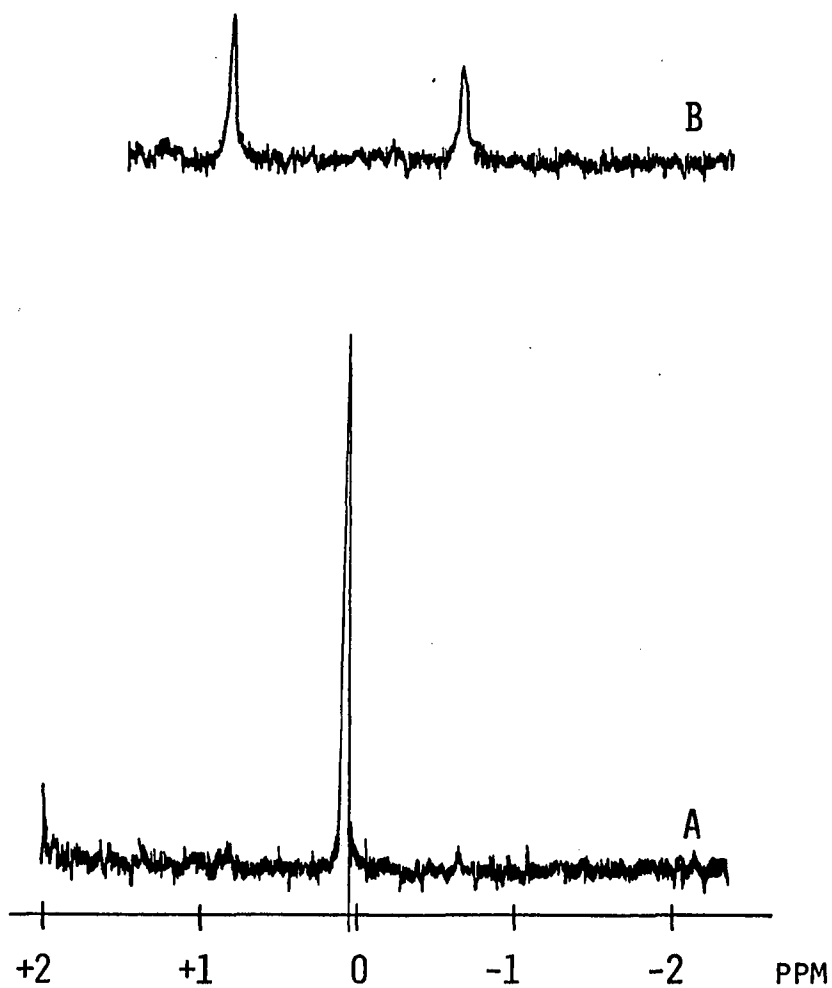


Figure 19. The ^{1}H-NMR spectrum between +2.0 and -2.0 of (A) $(CH_3)_2Co((l-)N_4)$ and (B) after the addition of Cd^{2+} (mole ratio = 0.5).

species present is $(CH_3)_2Cd$, the line broadening due to rapid intermolecular exchange is not observed.

Confirmation that CH_3Cd^+ is involved in the Schlenk-type equilibrium described above (eq 71) comes from studying the rate of methane evolution from solutions of Cd^{2+} and $(CH_3)_2Co(chel)$ (mole ratio $\geq$ 1.0). In contrast to CH_3Zn^+, CH_3Cd^+ does not appear to decompose by a simple process. Plots of $\ln(C_\infty - C)$ vs. time and $\ln[CH_3Cd^+]/[H_2O]$ vs. time were not linear. Therefore the decomposition is not the pseudo first- or second-order process that would be expected if CH_3Cd^+ were being hydrolyzed according to eq 72. Because both CH_3Cd^+ and $(CH_3)_2Cd$ can decompose to

$$CH_3Cd^+ + H_2O \longrightarrow Cd^{2+} + CH_4 + OH^- \qquad (72)$$

yield methane, and the concentrations of both organocadmium species are interrelated by the equilibrium, a complex rate law is necessary to describe fully the decomposition of CH_3Cd^+ and $(CH_3)_2Cd$ under the conditions of this study.

Reaction of $(CH_3)_2Co((1\text{-})N_4)$ with Pb^{2+}

In contrast to the reactions of $(CH_3)_2Co(chel)$ with Zn^{2+} and Cd^{2+}, the reaction of $(CH_3)_2Co(chel)$ with Pb^{2+} yielded some unexpected, but very interesting results. Because the two dimethyl complexes showed different reactivity toward Pb^{2+}, they will be discussed separately.

By analogy to the reactions of the dimethyl complexes with Zn^{2+} and Cd^{2+}, the reaction of $(CH_3)_2Co((1\text{-})N_4)$ with Pb^{2+} can occur with two different stoichiometries. Slow spectrophotometric titrations showed an endpoint of mole ratio = 0.50 (Figure 20), which is indicative of a reaction in which one mole of Pb^{2+} reacts with two moles of dimethyl complex (eq 73 and 74). Attempts were made to titrate the

$$(CH_3)_2Co((1\text{-})N_4) + Pb^{2+} \longrightarrow CH_3Co((1\text{-})N_4)^+ + CH_3Pb^+ \quad (73)$$

$$(CH_3)_2Co((1\text{-})N_4) + CH_3Pb^+ \longrightarrow CH_3Co((1\text{-})N_4)^+ + (CH_3)_2Pb \quad (74)$$

fast first reaction of the overall biphasic reaction (eq 73). These titrations did not, however, yield the expected 1.0 endpoint predicted by eq 73. The endpoint obtained was between 1.0 and 0.50 and reflects the partial reaction of CH_3Pb^+ formed in eq 73 with a second mole of the dimethyl complex (eq 74).

Solutions prepared from Pb^{2+} and excess $(CH_3)_2Co((1\text{-})N_4)$ in acetonitrile yielded a black precipitate. The solid was shown by nephelometry to precipitate immediately upon the addition of Pb^{2+}. The solid, which was identified by its X-ray powder diffraction pattern as lead metal, contained approximately 45% of the Pb^{2+} added. Tetramethyllead, $(CH_3)_4Pb$, was identified as the organolead product of the reaction by its resonance at +0.75 ppm in

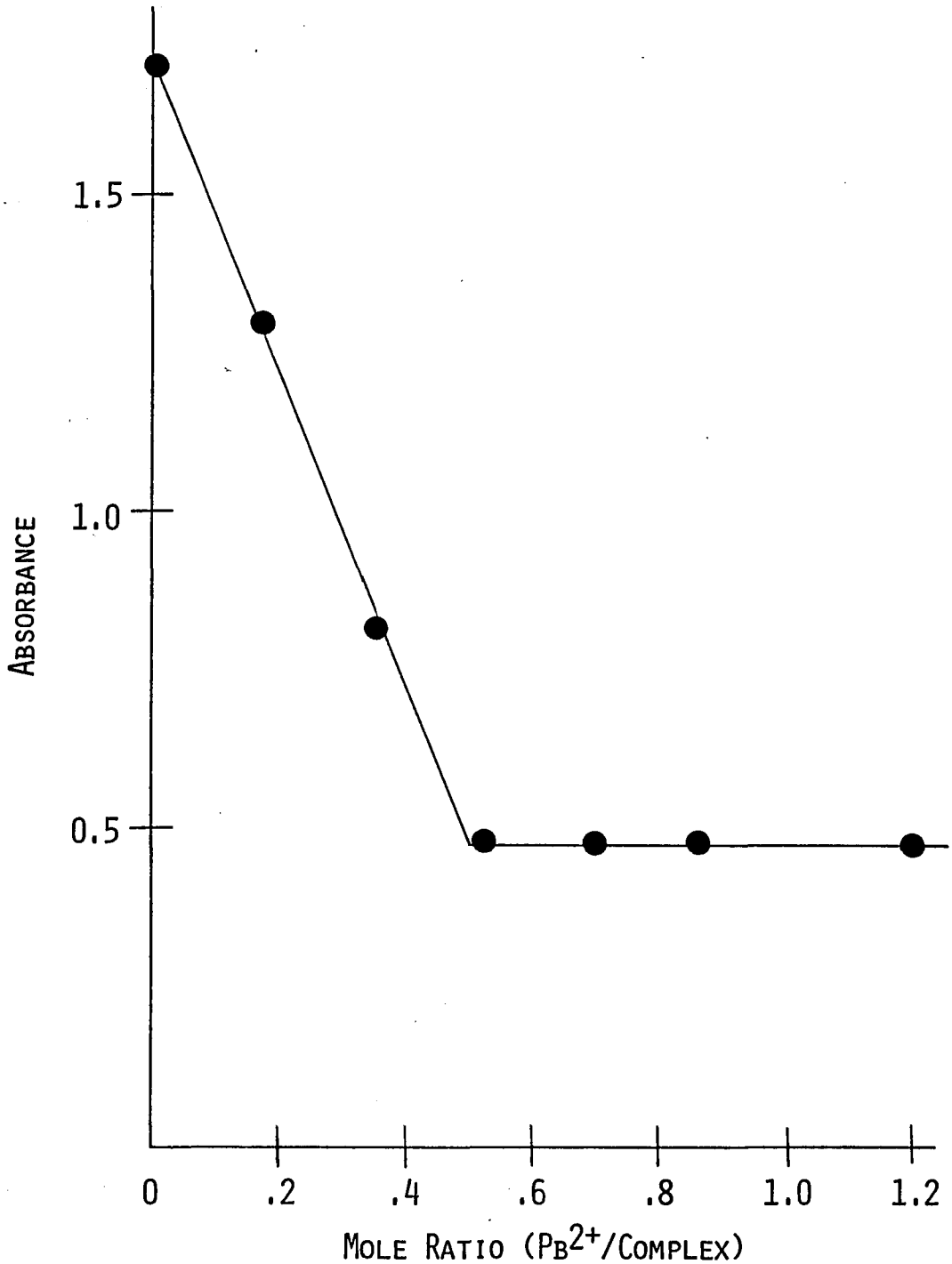


Figure 20. Representative spectral titration for the overall biphasic reaction of $(CH_3)_2Co((1\text{-})N_4)$ with Pb^{2+}.

the NMR spectrum of the reaction mixture. The assignment was confirmed by comparison to the spectrum of an authentic sample of $(CH_3)_4Pb$. GLC experiments demonstrated that approximately 49% of the Pb^{2+} added was converted to $(CH_3)_4Pb$. The GLC analysis also indicated that about 3% of the transferred methyl group formed methane.

The product analysis and spectrophotometric titrations suggest the following overall stoichiometry for the biphasic reaction (eq 75). The presence of equal amounts

$$2(CH_3)_2Co((1\text{-})N_4) + Pb^{2+} \xrightarrow{\text{fast}} 2[CH_3Co((1\text{-})N_4)]^+ + \tfrac{1}{2}(CH_3)_4Pb + \tfrac{1}{2}Pb^0 \quad (75)$$

of lead metal and lead(IV) in the product mixture implies that a lead(II) species is undergoing disproportionation. The literature (79, 119) suggests that either $(CH_3)_2Pb$ or CH_3Pb^+ could disproportionate to yield a methyllead(IV) species and lead metal (eq 76 and 77). The latter species,

$$(CH_3)_2Pb \longrightarrow \tfrac{1}{2}(CH_3)_4Pb + \tfrac{1}{2}Pb^0 \quad (76)$$

$$CH_3Pb^+ \longrightarrow \tfrac{1}{2}(CH_3)_2Pb^{2+} + \tfrac{1}{2}Pb^0 \quad (77)$$

CH_3Pb^+, has not been directly identified, but has been suggested as a possible intermediate in the biotransformation of Pb^{2+} to $(CH_3)_4Pb$ (79). Although there is no evidence that CH_3Pb^+ is susceptible to disproportionation, it was a possible reaction intermediate and as such needed to be considered. It is not possible to distinguish between

CH_3Pb^+ and $(CH_3)_2Pb$ as the unstable intermediate based on stoichiometry and product distribution.

If $(CH_3)_2Pb$ is the intermediate, then the scheme outlined in eq 80, 81, and 83 could occur. The unstable

$$(CH_3)_2Co((1\text{-})N_4) + Pb^{2+} \longrightarrow CH_3Pb^+ + CH_3Co((1\text{-})N_4)^+ \quad (80)$$

$$(CH_3)_2Co((1\text{-})N_4) + CH_3Pb^+ \longrightarrow (CH_3)_2Pb + CH_3Co((1\text{-})N_4)^+ \quad (81)$$

$$(CH_3)_2Pb \longrightarrow \tfrac{1}{2}(CH_3)_4Pb + \tfrac{1}{2}Pb^0 \quad (82)$$

intermediate CH_3Pb^+ results in the scheme outlined in eq 83, 84, 85, and 86. It is clear that both mechanisms would give the same reaction stoichiometry and product distribution.

$$(CH_3)_2Co((1\text{-})N_4) + Pb^+ \longrightarrow CH_3Pb^+ + CH_3Co((1\text{-})N_4)^+ \quad (83)$$

$$CH_3Pb^+ \longrightarrow \tfrac{1}{2}(CH_3)_2Pb^{2+} + \tfrac{1}{2}Pb^0 \quad (84)$$

$$\tfrac{1}{2}(CH_3)_2Co((1\text{-})N_4) + \tfrac{1}{2}(CH_3)_2Pb^{2+} \longrightarrow \tfrac{1}{2}(CH_3)_3Pb^+ + \tfrac{1}{2}CH_3Co((1\text{-})N_4)^+ \quad (85)$$

$$\tfrac{1}{2}(CH_3)_2Co((1\text{-})N_4) + \tfrac{1}{2}(CH_3)_3Pb^+ \longrightarrow \tfrac{1}{2}(CH_3)_4Pb + \tfrac{1}{2}CH_3Co((1\text{-})N_4)^+ \quad (86)$$

In order to differentiate between these mechanisms, a series of experiments was designed to determine whether

$(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$ were plausible intermediates. First, spectrophotometric titrations with $(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$ were performed to establish whether they would react with $(CH_3)_2Co((1\text{-})N_4)$ and whether the stoichiometry of the reaction was that predicted in eq 85 and 86. As shown in Figure 21, both methyllead salts behaved as expected: $(CH_3)_2Pb^{2+}$ underwent a 1:2 reaction with $(CH_3)_2Co((1\text{-})N_4)$ and $(CH_3)_3Pb^+$ underwent a 1:1 reaction with $(CH_3)_2Co((1\text{-})N_4)$.

NMR titrations with $(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$ confirmed the 1:2 and 1:1 reactions, respectively, and that $(CH_3)_4Pb$ was the final reaction product in both cases. What was needed, however, was direct observation of either $(CH_3)_2Pb^{2+}$, $(CH_3)_3Pb^+$, or $(CH_3)_2Pb$ in the solution prior to the appearance of $(CH_3)_4Pb$. Because the room-temperature reaction is too fast (i.e., the NMR shows $(CH_3)_4Pb$ immediately upon the addition of Pb^{2+}), the intermediates were sought during low temperature NMR experiments. Unfortunately, the freezing point of acetonitrile (-44°C) and the solubility of $(CH_3)_2Co((1\text{-})N_4)$ put a lower limit of -35°C on the study. During titrations with Pb^{2+}, $(CH_3)_2Pb^{2+}$, and $(CH_3)_3Pb^+$ the resonance peak for $(CH_3)_4Pb$ was observed immediately upon the addition of the titrant. There were no peaks attributable to the potential intermediates $(CH_3)_2Pb$, $(CH_3)_2Pb^{2+}$, or $(CH_3)_3Pb^+$, and on the basis of the NMR experiments no clear conclusion could be made concerning the mechanism of $(CH_3)_4Pb$ formation.

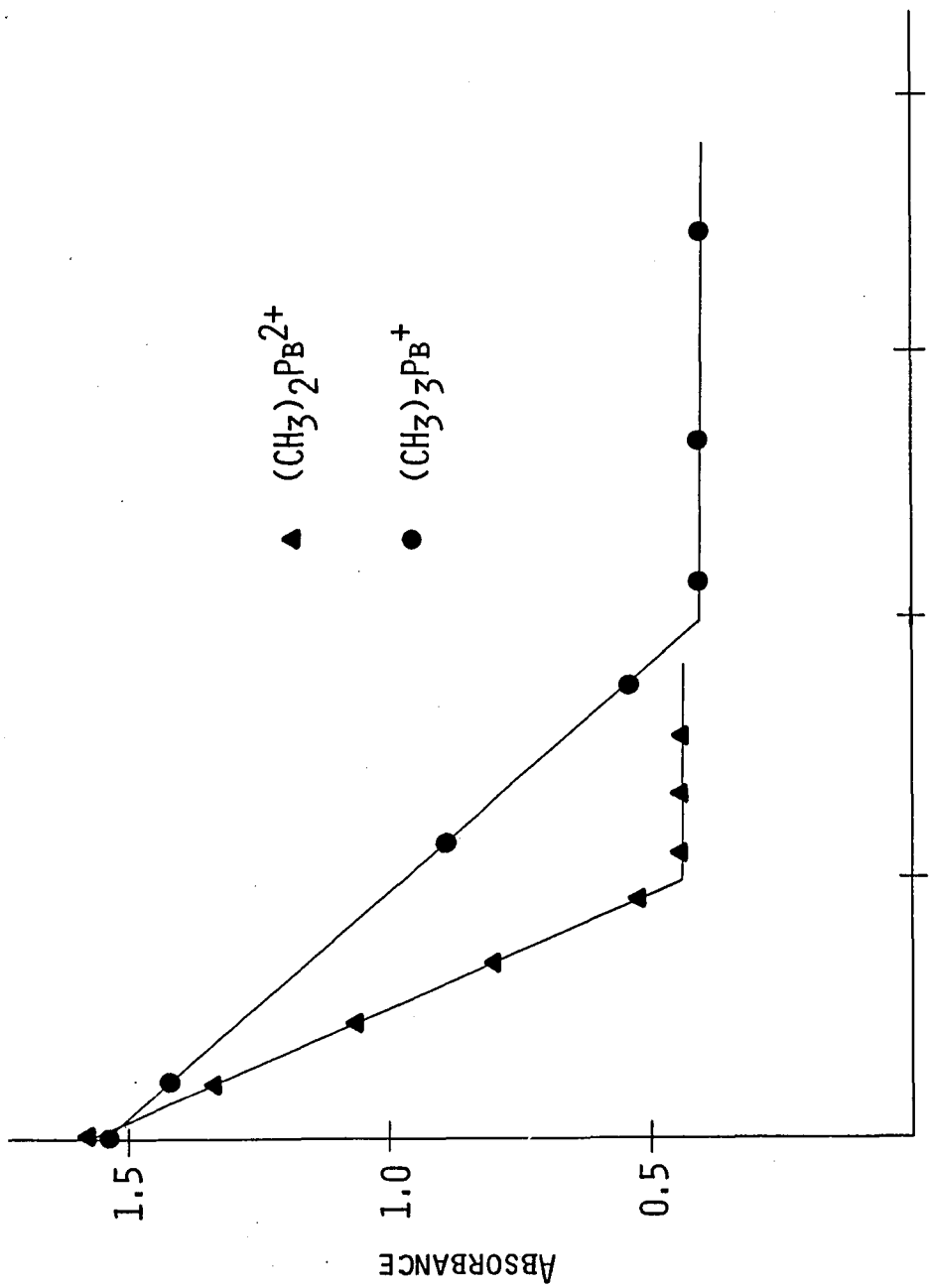


Figure 21. Representative spectral titration for the reaction of $(CH_3)_2Co((1\text{-})N_4)$ with $(CH_3)_3Pb^+$ (●) and $(CH_3)_2Pb^{2+}$ (▲).

Indirect evidence that $(CH_3)_2Pb$ is the unstable intermediate came from studies of the reaction between $(CH_3)_2Co((1\text{-})N_4)$ and excess Pb^{2+} (mole ratio $\geq$ 1.0). Under these conditions, only one methyl group can be transferred to Pb^{2+} (eq 87), so the chemistry of CH_3Pb^+ could be examined.

$$(CH_3)_2Co((1\text{-})N_4) + Pb^{2+} \longrightarrow CH_3Pb^+ + CH_3Co((1\text{-})N_4) \quad (87)$$

Addition of an equimolar quantity of Pb^{2+} to $(CH_3)_2Co((1\text{-})N_4)$ in acetonitrile results in a solution that contains a stoichiometric amount of $[CH_3Co((1\text{-})N_4)\text{-}(CH_3CN)]^+$, shows no precipitate, and evolves methane very slowly (although the addition of acid results in the immediate recovery of the theoretical amount of methane). This suggests that the CH_3Pb^+ presumably generated in this reaction is relatively stable. There is no evidence of disproportionation (eq 84).

The stability of CH_3Pb^+ in acetonitrile was determined by monitoring the rate of methane evolution by GLC. A plot of $\ln(C_\infty\text{-}C)$ vs. time was linear over several half-lives (Figure 22). From this data the half-life of the reaction was calculated to be 432 min (k_{obs} = 1.60 x 10^{-3} min^{-1}). This is consistent with a process in which CH_3Pb^+ is decomposed by water present from the hydrated Pb^{2+} (eq 88). Because the water is present in excess over the

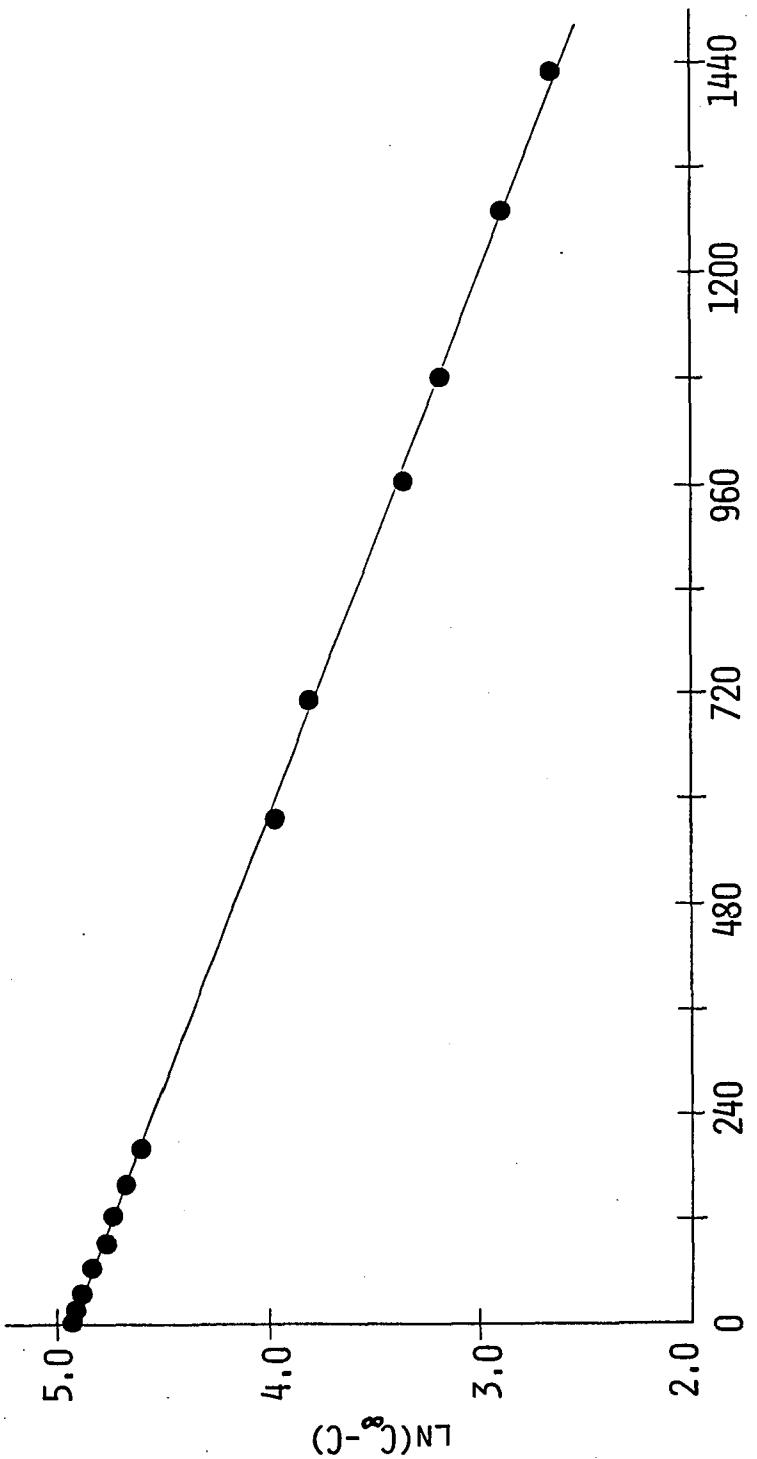


Figure 22. Rate of methane evolution for the reaction of $(CH_3)_2Co((1-)N_4)$ with Pb^{2+} (mole ratio = 4.0).

$$CH_3Pb^+ + H_2O \longrightarrow CH_4 + Pb^{2+} + OH^- \quad (88)$$

methyllead species, the reaction follows the observed pseudo first-order kinetics.

NMR studies to confirm the presence of CH_3Pb^+ in these solutions were carried out, as was done with CH_3Zn^+ and CH_3Cd^+. The NMR spectrum of a solution prepared from $(CH_3)_2Co((1\text{-})N_4)$ and excess Pb^{2+} (mole ratio > 1.0) consisted of the spectrum of $[CH_3Co((1\text{-})N_4)(CH_3CN)]^+$. There were no unexplainable peaks in the solution's NMR spectrum between -4.0 and +5.0 ppm. Because CH_3Pb^+ has never been characterized there is a problem of knowing where to look for the resonance due to CH_3Pb^+. One can make predictions about the possible resonance position of these compounds based on the known relationship between the electronegativity of X and the chemical shift of the methyl protons in CH_3-X compounds (120). Available data suggests that the chemical shift of the methyl protons in CH_3Pb^+ or $(CH_3)_2Pb$ might be expected to be in the area of 0 to +2.0 ppm. Careful reexamination of this region of the NMR spectra generated in this study did not reveal any new peaks. If, however, the chemical shift of the methyllead species was greater than +1.95 ppm, then it would be obscured by the resonances due to proton impurities in the solvent and the protons of the macrocycle (Figure 10).

Despite the failure to find direct evidence for the existence of an organolead(II) compound, all available

data, including the kinetics of methane evolution, the sensitivity of the species formed to acid, the indicated 1:1 reaction stoichiometry, and the similarity to the Zn^{2+} and Cd^{2+} chemistry, support the postulate that CH_3Pb^+ is indeed formed in these reactions.

Reaction of $[(CH_3)_2Co(N_4)]ClO_4$ with Pb^{2+}

The reaction of $[(CH_3)_2Co(N_4)]ClO_4$ with Pb^{2+} in acetonitrile is unique. The mechanism is apparently quite complex and not at all similar to any of the other mechanisms discussed previously.

Addition of an equimolar or excess amount of Pb^{2+} to $[(CH_3)_2Co(N_4)]^+$ in acetonitrile results in the quantitative conversion of the dimethyl to the monomethyl complex, $[CH_3Co(N_4)(CH_3CN)]^{2+}$. Observation of the UV-VIS spectrum of the reaction mixture indicates that the complex product is stable in the presence of the inorganic and organometallic lead products. This is suggestive of the 1:1 reaction shown in eq 89.

$$[(CH_3)_2Co(N_4)]^+ + Pb^{2+} \xrightarrow{CH_3CN} [CH_3Co(N_4)(CH_3CN)]^{2+} + CH_3Pb^+ \quad (89)$$

GLC analysis of the atmosphere over a solution prepared from $[(CH_3)_2Co(N_4)]^+$ and excess Pb^{2+} in acetonitrile showed that methane was evolved slowly. The rate of methane evolution was determined and a linear plot of

$\ln(C_\infty - C)$ vs. time (Figure 23) was obtained. From this data the half-life of the methane evolution was calculated to be 327 min (k_{obs} = 2.12 x 10^{-3} min^{-1}). This is consistent with the intermediate CH_3Pb^+ being decomposed by the water added as hydrated Pb^{2+} (eq 90). Because the water is in excess over the organometallic species, the reaction follows the observed pseudo first-order kinetics.

$$CH_3Pb^+ + H_2O \longrightarrow CH_4 + Pb^{2+} + OH^- \qquad (90)$$

In contrast to the reaction of $(CH_3)_2Co((1\text{-})N_4)$ with excess Pb^{2+}, the addition of excess Pb^{2+} to $[(CH_3)_2Co(N_4)]^+$ results in the immediate precipitation of a yellow solid. Although this compound is similar to PbO in appearance, its analysis did not support this formulation. The X-ray powder diffraction pattern obtained was consistent with PbI_2 but not with any of the lead oxides listed in the Powder Diffraction File (121). This suggests that the compound's structure is similar to PbI_2. Elemental analysis showed the compound to be approximately 40% lead by weight and to contain traces of carbon (2.9%), hydrogen (1.5%), and nitrogen (0.35%). The IR spectrum of the solid suggested that trace amounts of water and perchlorate might be present. Because the total amount of lead present in this compound approximates 5% of the Pb^{2+} used in the 1:1 reaction (eq 89), the unknown compound must be the product of a minor side reaction, and its identity was not pursued further.

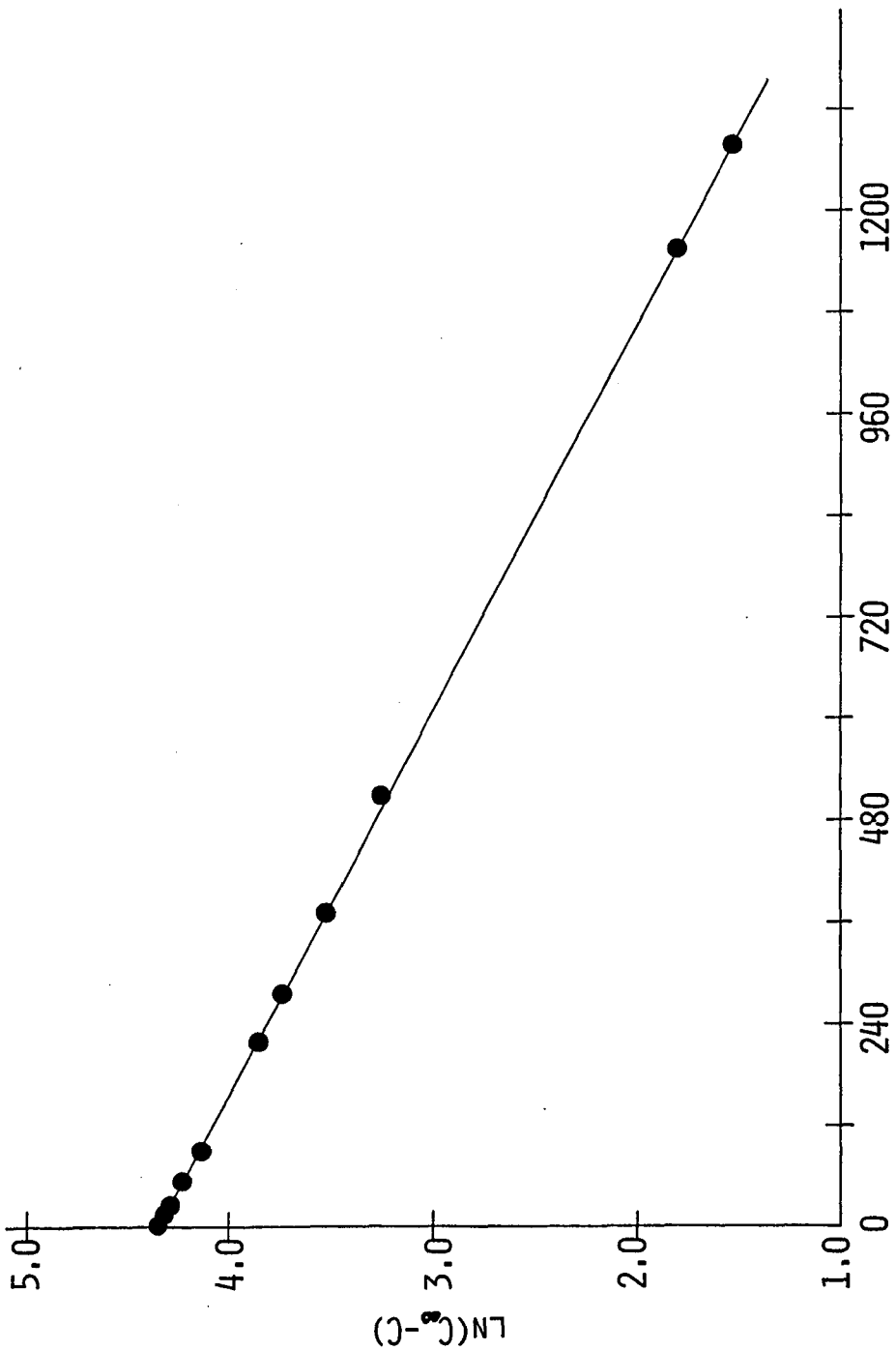


Figure 23. Rate of methane evolution for the reaction of $[(CH_3)_2Co(N_4)]^+$ with Pb^{2+} (mole ratio = 4.0).

^{1}H-NMR spectroscopy was used in an attempt to confirm the presence of the proposed CH_3Pb^+ intermediate. An examination of the NMR spectrum of a solution made from $[(CH_3)_2Co(N_4)]^+$ and excess Pb^{2+} revealed no resonances that could be attributed to CH_3Pb^+ or any other organolead species. Despite the absence of direct evidence for the existence of CH_3Pb^+, all other available data are consistent with an organometallic species of this formulation being produced in the 1:1 reaction of $[(CH_3)_2Co(N_4)]^+$ and Pb^{2+}.

Although the 1:1 reactions of $[(CH_3)_2Co(N_4)]^+$ with Pb^{2+} and $(CH_3)_2Co((1\text{-})N_4)$ with Pb^{2+} are similar, the reaction of Pb^{2+} with excess $[(CH_3)_2Co(N_4)]^+$ is quite different from the reaction of Pb^{2+} with excess $(CH_3)_2Co((1\text{-})N_4)$. Slow spectral titrations resulted in a titration curve that did not have a definite break (Figure 24). This suggests that the overall reaction probably does not have a well-defined stoichiometry.

Evidence to support the contention that the reaction does not occur in a well-defined manner was obtained from changes that occurred in the UV-VIS spectrum of $[(CH_3)_2Co(N_4)]^+$ as Pb^{2+} was added (Figure 25). It is clear that $[CH_3Co(N_4)(CH_3CN)]^{2+}$ is produced quantitatively, but there are two other features of the spectrum that are intriguing. First, no isosbestic points are present, and second, there is an absorbance at approximately 305 nm that is not present in the spectrum of $[CH_3Co(N_4)(CH_3CN)]^{2+}$.

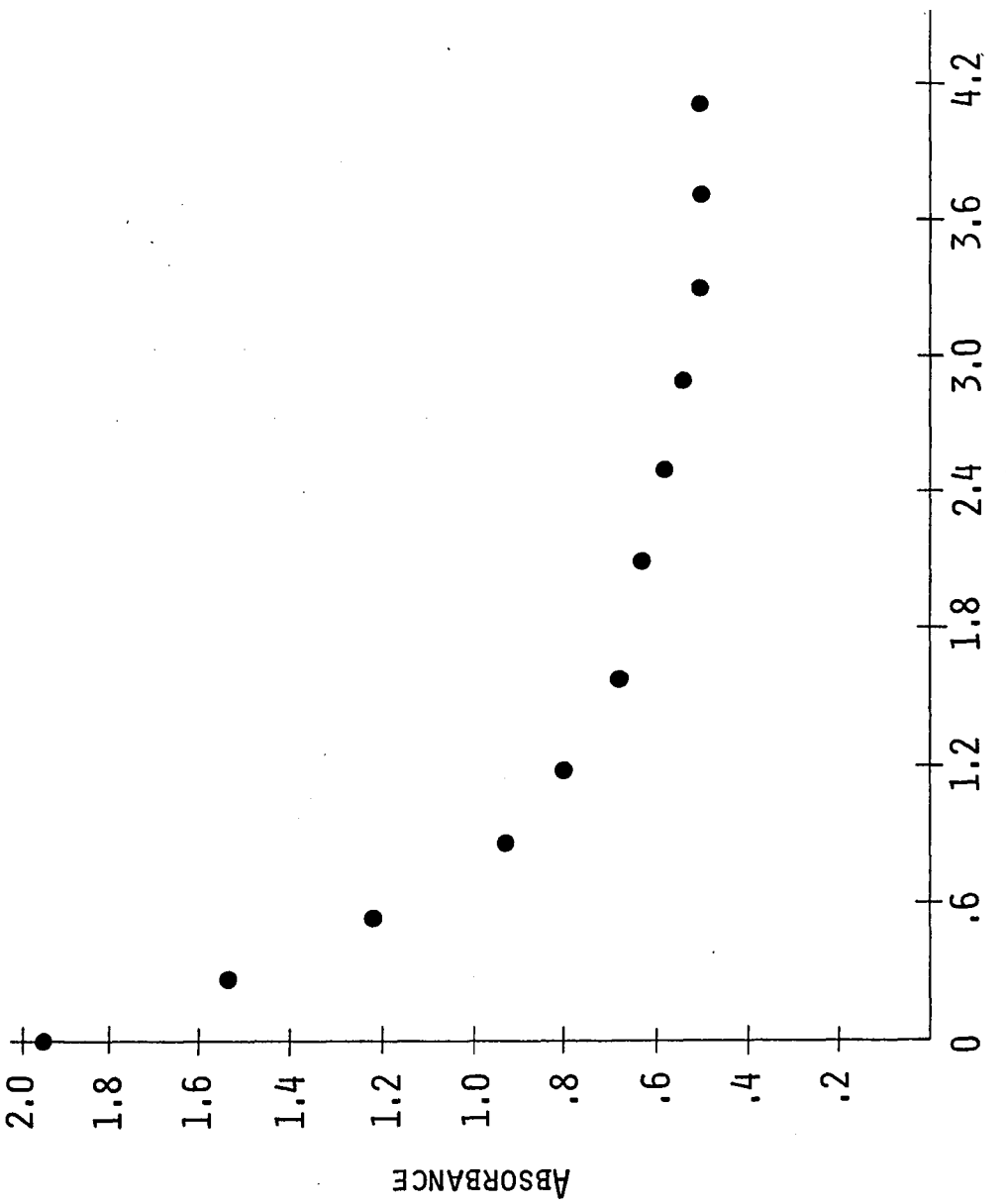


Figure 24. Representative spectral titration for the overall reaction of $[(CH_3)_2Co(N_4)]^+$ with Pb^{2+}.

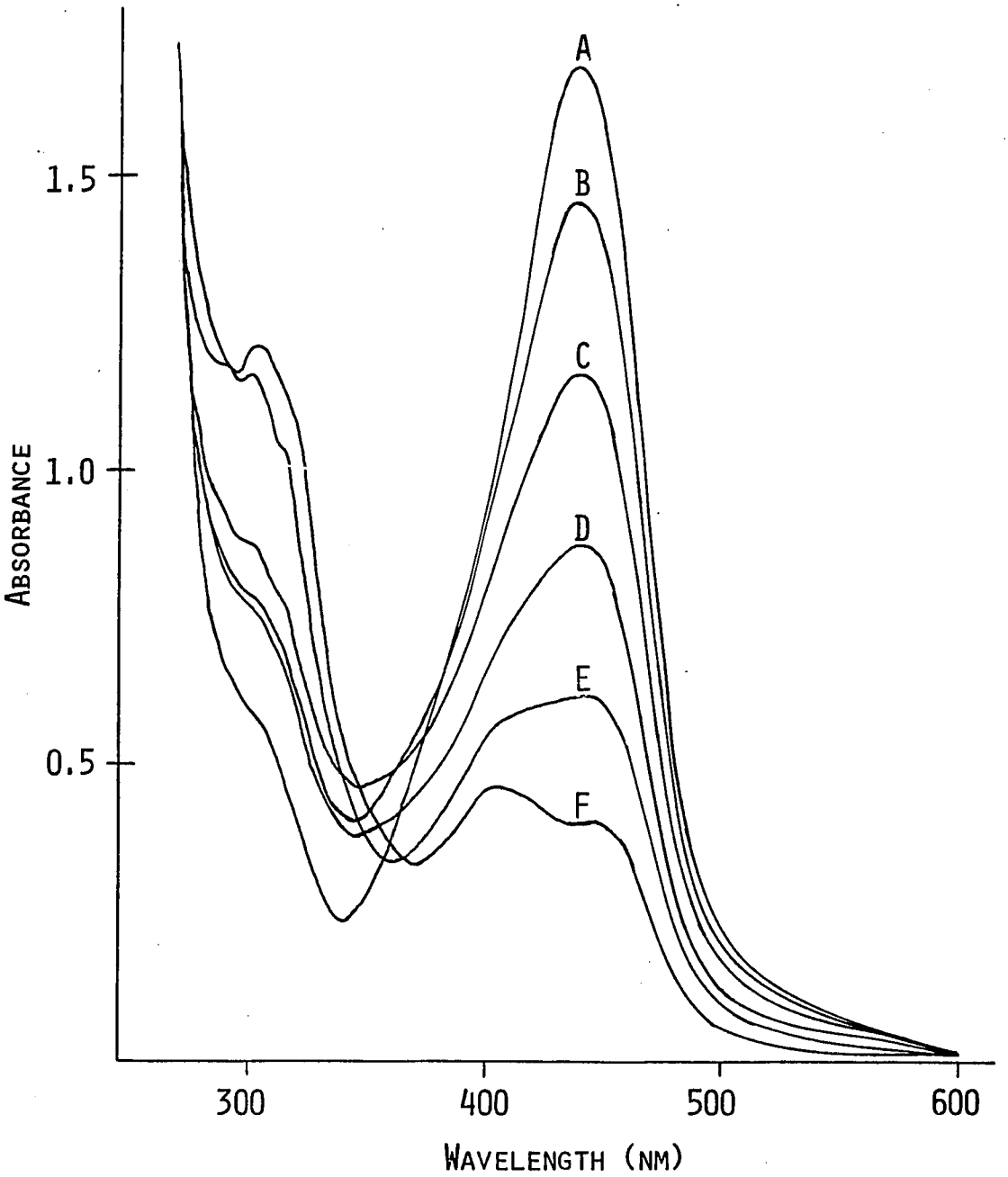


Figure 25. Changes in the UV-VIS spectrum (250-600 nm) of $[(CH_3)_2Co(N_4)]^+$ with the addition of Pb^{2+}. (A) No Pb^{2+} added; mole ratio = (B) 0.185, (C) 0.37, (D) 0.56, (E) 0.74, (F) 0.93.

The presence of isosbestic points is generally considered to be a reliable indication that the system under study contains only two absorbing species and that the reaction proceeds without any side reactions (122-125). Conversely, the absence of isosbestic points generally implies that the system under study contains more than two absorbing species and that there may be side reactions occurring. The overall reactions of $(CH_3)_2Co((1\text{-})N_4)$ with Pb^{2+} (eq 91) and $[(CH_3)_2Co(N_4)]^+$ with Zn^{2+} (eq 92) occur in a well-defined manner and the spectra of those reactions

$$2(CH_3)_2Co((1\text{-})N_4) + Pb^{2+} \longrightarrow 2[CH_3Co((1\text{-})N_4)]^+ + \tfrac{1}{2}Pb^0 + \tfrac{1}{2}(CH_3)_4Pb \quad (91)$$

$$2[(CH_3)_2Co(N_4)]^+ + Zn^{2+} \longrightarrow 2[CH_3Co(N_4)]^{2+} + (CH_3)_2Zn \quad (92)$$

exhibit isosbestic points (Figures 26 and 27). The absence of isosbestic points in Figure 25 strongly suggests that something more complex than expected is occurring. Additional support for this conclusion is the presence of an absorbance at 305 nm in the spectrum of the titration (Figure 25). Comparison with the spectrum of $[CH_3Co(N_4)(CH_3CN)]^{2+}$ shown in Figure 28 makes it clear that another chromophore is present.

As was found in the reaction of Pb^{2+} with excess $(CH_3)_2Co((1\text{-})N_4)$, the reaction of Pb^{2+} with excess $[(CH_3)_2Co(N_4)]^+$ produces lead metal, $(CH_3)_4Pb$, and a small

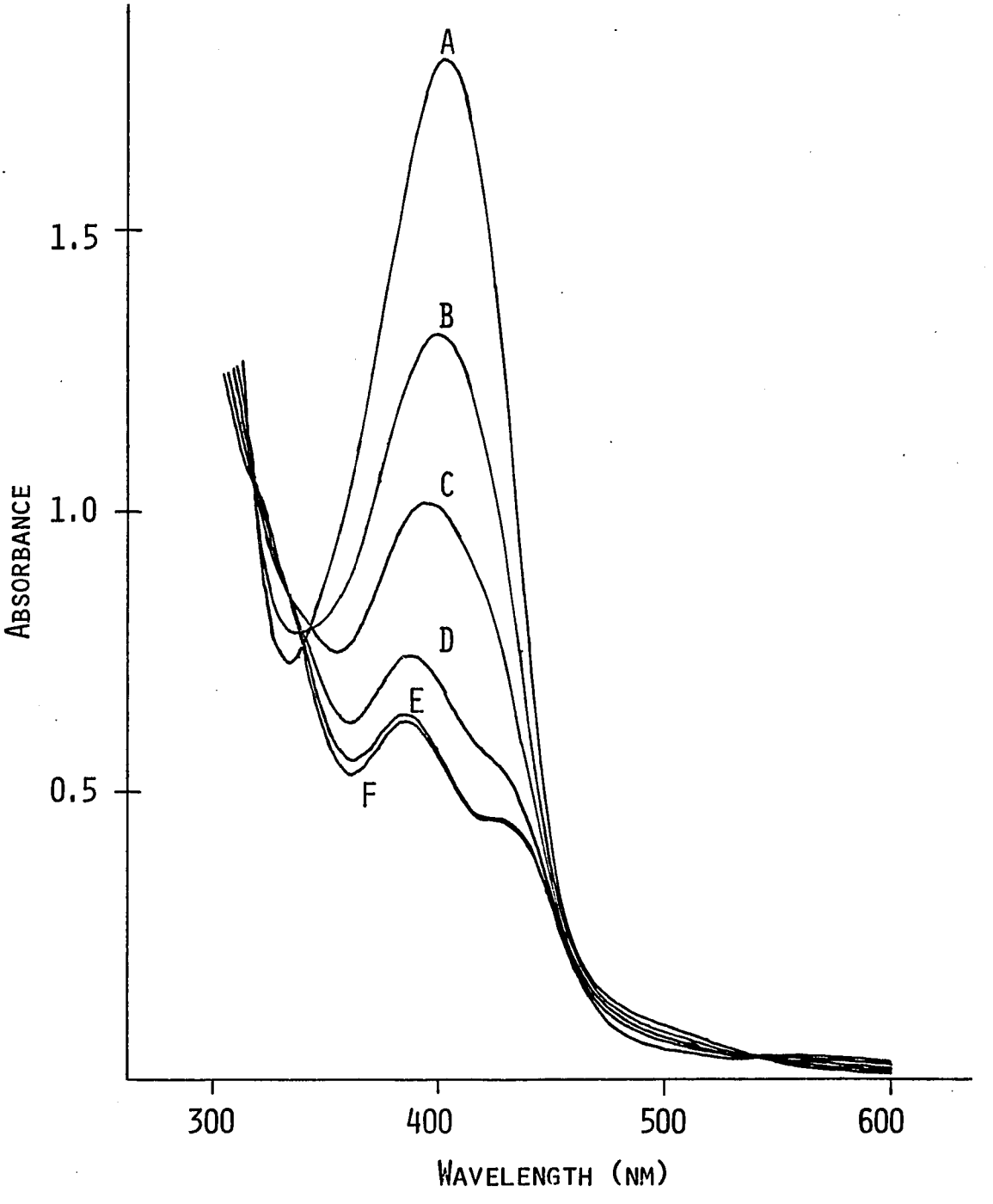


Figure 26. Changes in the UV-VIS spectrum (250-600 nm) of $(CH_3)_2Co((1\text{-})N_4)$ with addition of Pb^{2+}. (A) No Pb^{2+} added; mole ratio = (B) 0.12, (C) 0.24, (D) 0.36, (E) 0.48, (F) 0.60.

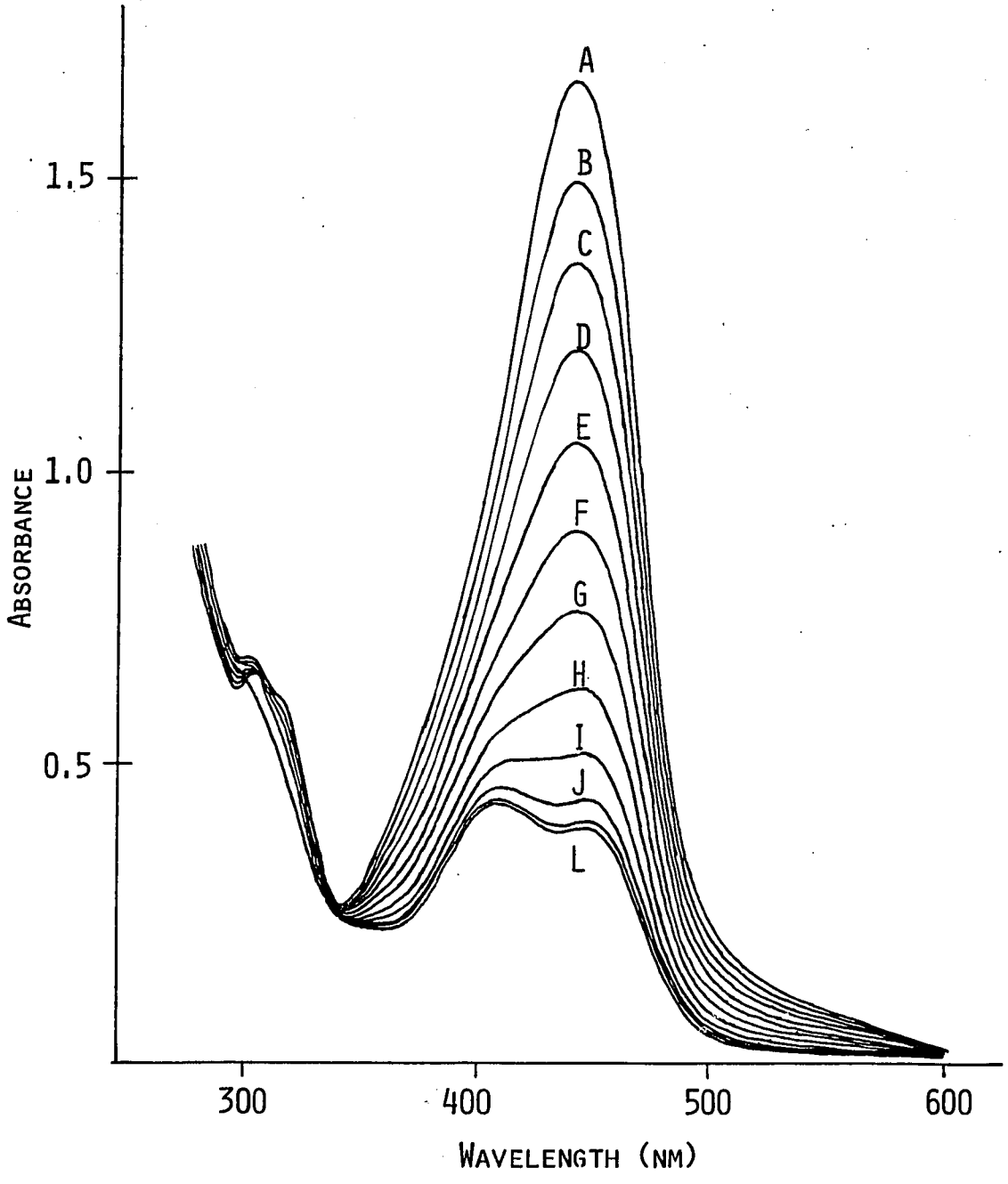


Figure 27. Changes in the UV-VIS spectrum (250-600 nm) of $[(CH_3)_2Co(N_4)]^+$ with addition of Zn^{2+}. (A) No Zn^{2+} added; mole ratio = (B) 0.05, (C) 0.10, (D) 0.15, (E) 0.20, (F) 0.25, (G) 0.30, (H) 0.35, (I) 0.40, (J) 0.45, (K) 0.50, (L) 0.55.

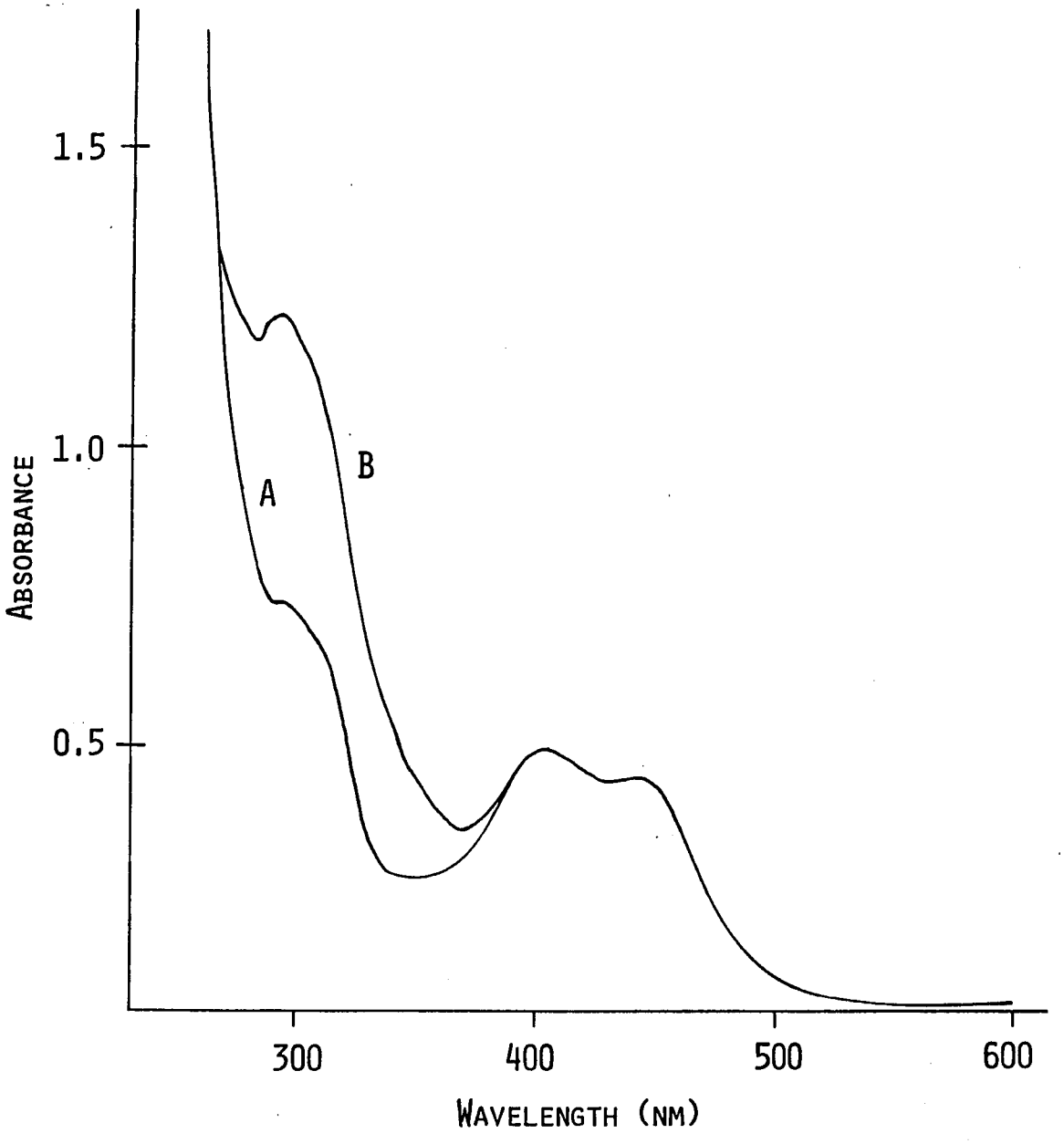


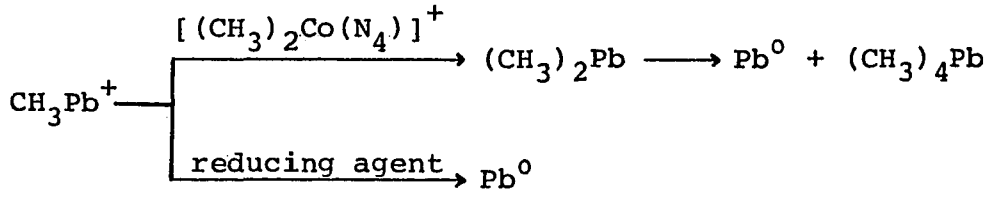
Figure 28. The UV-VIS spectrum (200-700 nm) of (A) $[CH_3Co(N_4)(CH_3CN)]^{2+}$ and (B) solution of $[(CH_3)_2Co(N_4)]^{+}$ after titration with Pb^{2+}.

quantity of methane. It is unusual, however, that of the Pb^{2+} added, approximately 75% is found as lead metal and approximately 10% as $(CH_3)_4Pb$. Based on previous results, it is expected that for every mole of $(CH_3)_4Pb$ obtained, one mole of lead metal will be found. Since only 10% of the lead is found as $(CH_3)_4Pb$, only 10% of the lead should appear as Pb^0. The presence of extra lead metal suggests that there is a reducing agent in the system.

The results from the reaction of $[(CH_3)_2Co(N_4)]^+$ with excess Pb^{2+} indicate that the 1:1 reaction (eq 93) occurs in the expected manner (except for a minor side reaction

$$[(CH_3)_2Co(N_4)]^+ + Pb^{2+} \longrightarrow [CH_3Co(N_4)]^{2+} + CH_3Pb^+ \quad (93)$$

as noted). Thus it can be assumed that the 1:1 reaction occurs normally when the dimethyl complex is in excess. What this suggests, then, is that there are at least two different pathways by which CH_3Pb^+ can react in the presence of excess $[(CH_3)_2Co(N_4)]^+$, as shown in Scheme I.



Scheme I

First, as in the reaction of $(CH_3)_2Co((1\text{-})N_4)$ and CH_3Pb^+, a second methyl group can be transferred to form $(CH_3)_2Pb$, which disproportionates to form $(CH_3)_4Pb$ and Pb^0. The second pathway involves the reduction of CH_3Pb^+ to lead metal. Apparently the reduction occurs in preference to methylation, as is evidenced by the small amount of $(CH_3)_4Pb$ produced. Espenson and coworkers (68) demonstrated that $(CH_3)_2Co((1\text{-})N_4)$ reacts much more rapidly with electrophiles such as $C_6H_5Hg^+$ and H_3O^+ than does $[(CH_3)_2Co(N_4)]^+$. Thus the reduction of CH_3Pb^+ may be occurring because of the slow kinetics of the second methyl transfer.

The question then becomes two-fold. What is the identity of the reducing agent, and what is the fate of the methyl group that was transferred to the lead? From the studies on the 1:1 reaction of $[(CH_3)_2Co(N_4)]^+$ and Pb^{2+} it is apparent that $[CH_3Co(N_4)]^{2+}$, ClO_4^-, H_2O, and CH_3CN do not act as reducing agents toward CH_3Pb^+. The only other species present in these solutions whose reactivity toward CH_3Pb^+ cannot be fully accounted for is $[(CH_3)_2Co(N_4)]^+$.

If $[(CH_3)_2Co(N_4)]^+$ were acting as a reducing agent toward CH_3Pb^+, then an organolead(IV) complex, such as $[(CH_3)_2Co^{IV}(N_4)]^{2+}$, would be produced. Because Co^{IV} is paramagnetic, this hypothesis could be tested by monitoring the progress of the reaction with EPR spectroscopy.

If a Co^{IV} intermediate were formed, its characteristic 8 line EPR spectrum (126) should be quite obvious. However, the EPR spectrum of a solution made from Pb^{2+} and excess $[(CH_3)_2Co(N_4)]^+$ showed no evidence for any paramagnetic species at 77K. The stability of bisorganocobalt(IV) complexes is unknown, and if one were present it might decompose before it could be detected. Known organocobalt(IV) complexes (126) decompose by loss of either a carbocation (R^+) or a radical ($R\cdot$) as shown in Scheme II. The products of both of these decompositions would be observable

$$RCo^{IV}(chel) \longrightarrow Co^{III}(chel) + R\cdot$$
$$RCo^{IV}(chel) \longrightarrow Co^{II}(chel) + R^+$$

Scheme II

inasmuch as Co^{II} is paramagnetic and the radical would be expected to abstract a hydrogen atom and produce a hydrocarbon. Because neither observation was made, it is concluded that a Co^{IV} species is not involved in this reaction.

If radical intermediates are not involved in the reduction of CH_3Pb^+, then the only logical mechanism not yet considered is reductive elimination (eq 94). This decomposition pathway requires a nucleophile (X) to be

$$CH_3PbX \longrightarrow Pb^0 + CH_3X \qquad (94)$$

present. Because there are no nucleophiles present, however, this mechanism also seems improbable.

As was mentioned above, the amount of excess Pb^0 found is equal to the amount of transferred methyl that is missing. Acidification of the reaction mixture does not yield additional methane or any other volatiles. This would suggest that the missing methyls have been incorporated into a stable organic compound. If they were still associated with a metal center, this treatment would produce methane. Examination of the NMR spectrum of a solution prepared from Pb^{2+} and excess $[(CH_3)_2Co(N_4)]^+$, however, did not reveal anything of interest other than the expected spectrum of $[CH_3Co(N_4)]^+$ and the small quantity of $(CH_3)_4Pb$ that is produced.

The results obtained from the reaction of $[(CH_3)_2Co(N_4)]ClO_4$ with Pb^{2+} do not lend themselves to an unambiguous interpretation of the mechanism of this reaction. The more logical conclusions concerning possible reaction intermediates and pathways have been pursued, but they do not appear to fit the experimental observations.

Reaction of $(CH_3)_2Co((1\text{-})N_4)$ with Cr^{3+} and Cu^{2+}

The reactions of $(CH_3)_2Co((1\text{-})N_4)$ with Cr^{3+} and Cu^{2+} were briefly examined as part of a survey designed to identify potentially interesting reactions. Time constraints prohibited a detailed study, but the preliminary

results demonstrate that both reactions merit further study.

The stoichiometry of the reaction between Cr^{3+} and $(CH_3)_2Co((1\text{-})N_4)$ in acetonitrile was established by spectral titration. These titrations show a 1:1 endpoint, which is suggestive of the formation of CH_3Cr^{2+} (eq 95).

$$(CH_3)_2Co((1\text{-})N_4) + Cr^{3+} \longrightarrow CH_3Co((1\text{-})N_4)^+ + CH_3Cr^{3+} \quad (95)$$

Well-known organochromium compounds of the general formula $[RCr(H_2O)_5]^{2+}$ (R = CH_3, C_6H_5, CH_2, etc.) (127) tend to show moderate stability in solution but are sensitive to oxygen. It was quite surprising, then, when GLC experiments showed that 100% of the theoretical methane is evolved from an anaerobic solution of $(CH_3)_2Co((1\text{-})N_4)$ upon the addition of an equimolar or excess amount of Cr^{3+}. The sensitivity of CH_3Cr^{2+} to oxygen has been noted, but if oxygen is causing the decomposition, the expected product would be formaldehyde, not methane (eq 96).

$$CH_3Cr^{2+} \xrightarrow{O_2} Cr^{3+} + CH_2O \quad (96)$$

The reaction of Cu^{2+} with $(CH_3)_2Co((1\text{-})N_4)$ in acetonitrile appears to proceed in a manner similar to that observed by Witman (69) for the reaction of Ag^+ and $(CH_3)_2Co((1\text{-})N_4)$. Spectrophotometric titrations showed a variable endpoint of less than 1.0. GLC experiments showed that the addition of an equimolar amount of Cu^{2+}

to a solution of $(CH_3)_2Co((1\text{-})N_4)$ resulted in the instantaneous evolution of both ethane and methane in a 9:1 ratio. This can be explained in terms of the intermediate CH_3Cu^+ (eq 97) decomposing by either intermolecular reductive elimination (eq 98) (128, 129) (major pathway) or homolytic bond cleavage (eq 99) with the methyl radical abstracting

$$(CH_3)_2Co((1\text{-})N_4) + Cu^{2+} \longrightarrow [CH_3Co((1\text{-})N_4)]^+ + CH_3Cu^+ \quad (97)$$

$$2CH_3Cu^+ \longrightarrow 2Cu^+ + C_2H_6 \quad (98)$$

$$CH_3Cu^+ \longrightarrow CH_3\cdot + Cu^+$$
$$CH_3\cdot \xrightarrow{H\cdot} CH_4 \quad (99)$$

a hydrogen atom to form methane. The fact that the endpoints are less than 1.0 suggests that the intermediate Cu^+ reacts with a second mole of $(CH_3)_2Co((1\text{-})N_4)$ to produce CH_3Cu (eq 100).

$$(CH_3)_2Co((1\text{-})N_4) + Cu^+ \longrightarrow [CH_3Co((1\text{-})N_4)]^+ + CH_3Cu \quad (100)$$

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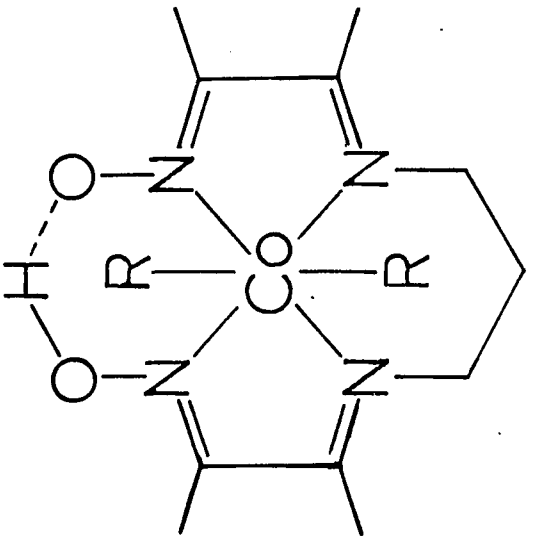
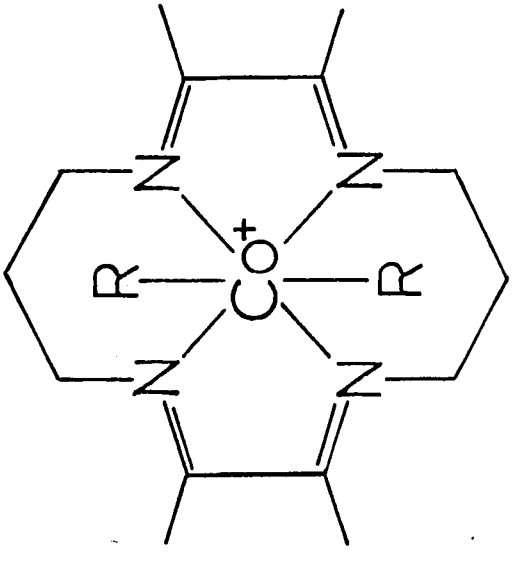
APPENDIX

STRUCTURES OF DIALKYLCOBALT COMPLEXES

(R = CH_3 IN THIS STUDY)



$R_2Co((1-)N_4$



$R_2\ Co(N_4)^+$